Electronic Supplementary Material (ESI) for Green Chemistry.


Supporting Information

# Hydration and Alkoxylation of Alkynes Catalyzed by NHC-Au-OTf

*Mattia Gatto,[a] Walter Baratta,[a] Paola Belanzoni,[b][c][d]* Leonardo Belpassi,[c][d], Alessandro Del Zotto,[a] Francesco Tarantelli,[b][c][d] Daniele Zuccaccia,[a][c]**

[a] Dipartimento di Scienze Agroalimentari, Ambientali e Animali, Sezione di Chimica, Università di Udine, Via Cotonificio 108, I-33100 Udine, Italy;
[b] Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, I-06123, Perugia, Italy
[c] Istituto di Scienze e Tecnologie Molecolari del CNR (CNR-ISTM), c/o Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, I-06123, Perugia, Italy;
[d] Consortium for Computational Molecular and Materials Sciences (CMS)$^2$, Via Elce di Sotto 8, I-06123, Perugia, Italy

Corresponding Author
* D. Z. E-mail: daniele.zuccaccia@uniud.it.
* P. B. E-mail: paola.belanzoni@unipg.it.

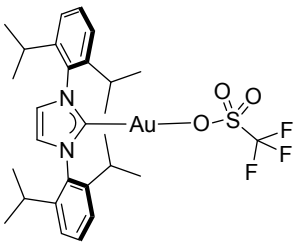
# Supporting Information

## 1. GENERAL PROCEDURES AND MATERIALS

$HAuCl_4$, tetrahydrothiophene (THT), and alkynes (3-hexyne, 3-phenyl-1-propyne, 1-phenyl-1-propyne, phenylacetylene and diphenylacetylene) were purchased from Sigma Aldrich. All the solvents (Table 1 of the manuscript) were used as delivered without any further purification unless otherwise specified.

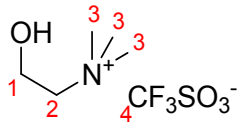
## 2. SYNTHESIS

1,3-bis(diisopropylphenyl)imidazolium chloride (NHC),[1] (THT)AuCl,[2] NHC-Au-Cl,[3] (NHC)-Au-(CH2COCH3), [4](NHC)-Au-OTf, and NHC-Au-(3-hexyne)$SbF_6$[5] were synthesized according to the literature. All compounds were characterized in solution by $^1H$ and $^{13}C$ spectroscopies. Spectra were measured on Bruker AC200 spectrometer. Referencing is relative to TMS ($^1H$ and $^{13}C$). The elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer.




**NHC-Au-OTf**

The synthesis follows an already known procedure.[6] In a schlenk flask 1 equiv. (319 mg, 0.50 mmol) of (NHC)-Au-($CH_2COCH_3$) and 1,1 equiv. (48.21 μL, 0.55 mmol) of trifluoromethanesulfonic acid were added to 5 mL of chloroform.. The reaction was stirred at ambient temperature for 3 hours. The solution was filtered through a paddle of Celite and the solvent was removed under vacuum. The residue was dissolved with a minimum quantity of $CH_2Cl_2$ and precipitated with n-pentane. The product was collected by filtration, washed with n-pentane (2 x 2 mL) and dried under vacuum. The white microcrystalline product was obtained with a yield of 85.1%. NMR and elemental analysis data are in accordance with the literature.




**Choline trifluoromethan sulfonate**

In a schlenk flask under argon 1 equivalent of choline chloride (1 g, 7.16 mmol), previously dried at 80 °C in oven overnight, was dissolved in 5 mL of dry acetonitrile. The mixture was kept agitated with a magnetic

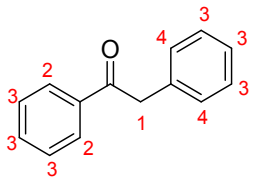
stir bar at ambient temperature and 1.1 equivalents of methyl trifluoromethansulfonate (891.6 mL, 7.88 mmol) were slowly added. The reaction was stirred at ambient temperature for 2 hours, the solvent was removed under reduced pressure and the residue was kept under vacuum overnight. The reaction gave a white powder, 172.3 mg, yield 95%. $^{1}$H NMR (200 MHz, $D_2O$, ppm) δ 4.08-3.96 (m, 1, 2H), 3.51-3.43 (m, 2, 2H), 3.16 (s, 3, 9H); $^{13}$C NMR (200 MHz, $D_2O$, ppm): δ 131.69, 125.94, 125.39, 119.08, 70.03, 69.97, 69.91, 58.16, 56.49, 56.42, 56.34 (3). Found: C, 28.3; H, 5.9; N, 25.8; S, 12.8. Calc. for $C_6H_{14}F_3NO_4S$: C, 28.5; H, 5.6; N, 25.3; S, 12.7%.

## 3. CATALYSIS

**Methoxylation of 3-hexyne (Table 1 of the manuscript)**.

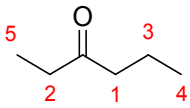
NHC-Au-OTf (1.62 mg, 0.0022 mmol), anhydrous methanol (89 µL, 2.2 mmol), 3-hexyne (125 µL, 1.1 mmol) and 200 µL of the solvent were added into a 2 mL glass screw-top vial. Using DES as solvent: cholinetriflate\dimethylurea (0.47\0.95 mmol, 120\84 mg) or citric acid\dimethylurea (0.64\0.96 mmol, 122.6\84.3 mg). The vial was placed in a bath oil at 30°C with magnetic stirring. The reactions were checked by NMR: 10 µL of the reaction mixture was added to a 500 mL of non-anhydrous $CDCl_3$. The progress of the reaction was monitored integrating the signal of 3-hexanone formed by hydrolysis of the product 3,3-dimethoxyhexane (due to adventitious water present in $CDCl_3$) and 3-hexyne. Conversion was calculated from the integral intensities of the corresponding signals (conversion [%] = (n 3-hexanone) / (n 3-hexyne + n 3-hexanone) x 100).Reported yields are an average of three runs.

**Hydration of diphenylacetylene (Table S1)**.



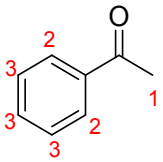

NHC-Au-OTf (from 0.000025 to 0.0025 mmol), diphenylaceteylene (89 mg, 0.5 mmol), water (9.9 µL, 0.55 mmol) and 240.1 µL of γ-valerolactone were added into a 2 mL glass screw-top vial,. The vial was placed in a bath oil at 120-80-50 °C with magnetic stirring. The reactions were checked by NMR: 10 µL of the reactions mixture was added to a 500 mL of non-anhydrous $CDCl_3$. The progress of the reaction was monitored integrating the signal of 1,2-diphenylethanone and diphenylaceteylene. Conversion was calculated from the integral intensities of the corresponding signals (conversion [%] = (n 1,2-diphenylethanone) / (n diphenylaceteylene + n 1,2-diphenylethanone) x 100). Reported yields are an average of three runs. $^1H$ NMR (200 MHz, $CDCl_3$, ppm): δ 8.01 (m, **2**), 7.62-7.39 (m, **3**), 7.31-7.27 (m, **4**), 4.28 (s, **1**).

**Hydration of 3-hexyne (Table S2)**.



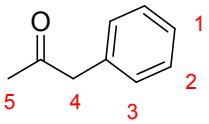

NHC-Au-OTf (1.29 mg, 0.00175 mmol), 3-hexyne (199 μL, 1.75 mmol), water (34.65 μL, 1.925 mmol) and 200 μL of γ-valerolactone were added into a 2 mL glass screw-top vial,. The vial was placed in a bath oil at 30 °C with magnetic stirring. The reactions were checked by NMR: 10 μL of the reactions mixture was added to a 500 mL of non-anhydrous $CDCl_3$. The progress of the reaction was monitored integrating the signal of 3-hexanone and 3-hexyne. Conversion was calculated from the integral intensities of the corresponding signals (conversion [%] = (n 3-hexanone) / (n 3-hexyne + n 3-hexanone) x 100). Reported yields are an average of three runs. $^1$H NMR (200 MHz, $CDCl_3$, ppm): δ 2.49-2.26 (m, **2-1**), 1.60 (q, $^3J_{HH}$ =7.4 Hz, **3**), 1.02 (s, **5**), 0.89 (s, **4**).

**Hydration of phenylacetylene (Table S2)**.




NHC-Au-OTf (from 0.0005 to 0.0025 mmol), phenylaceteylene (55 μL, 0.5 mmol), water (9.9 μL, 0.55 mmol) and 185.1 μL of γ-valerolactone were added into a 2 mL glass screw-top vial,. The vial was placed in a bath oil at 120, 80 or 50 °C with magnetic stirring. The reactions were checked by NMR. Conversion was calculated from the integral intensities of the corresponding signals. Reported yields are an average of three runs. $^1$H NMR (200 MHz, $CDCl_3$, ppm): δ 8.00-7.91 (m, **2**), 7.63-7.41 (m, **3**), 2.62 (s, **1**)

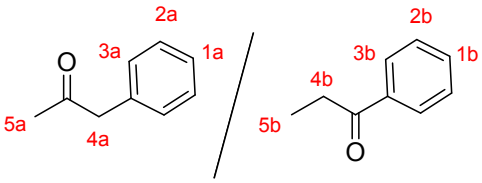
**Hydration of 3-phenyl-1-propyne (Table S2)**.




NHC-Au-OTf (0.73 mg, 0.001 mmol), 3-phenyl-1-propyne (124 μL, 1 mmol), water (19.8 μL, 1.1 mmol) and 106.2 μL of γ-valerolactone were added into a 2 mL glass screw-top vial,. The vial was placed in a bath oil at 120 °C with magnetic stirring. The

reactions were checked by NMR. Conversion was calculated from the integral intensities of the corresponding signals. Reported yields are an average of three runs. $^{1}$H NMR (200 MHz, $CDCl_3$, ppm): δ 7.97 (m, **1-2-3**), 3.70 (s, **4**), 2.15 (s, **5**)

**Hydration of 1-phenyl-1-propyne (Table S2)**.




NHC-Au-OTf (0.73 mg, 0.001 mmol), 1-phenyl-1-propyne (125 μL, 1 mmol), water (19.8 μL, 1.1 mmol) and 105.2 μL of γ-valerolactone were added into a 2 mL glass screw-top vial,. The vial was placed in a bath oil at 120 °C with magnetic stirring. The reactions were checked by NMR. Conversion was calculated from the integral intensities of the corresponding signals. Reported yields are an average of three runs. $^{1}$H NMR (200 MHz, $CDCl_3$, ppm): δ 8.01-7.93 (m, **3b**), 7.62-7.36 (m, **1b-2b**), 7.35-7.16 (m, **1a-2a-3a**), 3.70 (s, **4a**), 3.01 (q, $^{3}J_{HH}$ =7.21 Hz, **4b**), 2.15 (s, **5a**), 1.23 (t, $^{3}J_{HH}$ =7.25 Hz, **5b**)

**Table S1**: NHC-Au-OTf catalyzed hydration of diphenylacetylene in γ-valerolactone.[a]

| Entry | Temp(°C) | Loading (mol %)[b] | Conv (%)[c] | Time[d](h) | TOF[e] ($h^{-1}$) |
|---|---|---|---|---|---|
| 1 | 120 | 0.1 | 76 | 1 | 760 |
| | | | 95 | 2 | 475 |
| | | | 97 | 3 | 323 |
| | | | 99 | 3.5 | 283 |
| 2 | | 0.05 | 14.8 | 2 | 148 |
| | | | 15 | 6 | 50 |
| | | | 18.2 | 24 | 15 |
| | | | 21.9 | 30 | 15 |
| 3 | | 0.02 | 0 | 2 | 0 |
| | | | 0 | 9 | 0 |
| | | | 0 | 30 | 0 |
| | | | 0 | 72 | 0 |
| 4 | 80 | 0.25 | 30.1 | 1 | 120 |
| | | | 63.5 | 3 | 85 |
| | | | 82.8 | 5.5 | 60 |
| | | | 85.8 | 7 | 49 |
| | | | 88.4 | 24 | 15 |
| 5 | 50 | 0.5 | 26.8 | 1 | 54 |
| | | | 40.5 | 2 | 41 |
| | | | 77.8 | 5 | 31 |
| | | | 85.9 | 6 | 25 |
| | | | 90.3 | 9 | 20 |
| 6 | | 0.25 | 10.5 | 1 | 42 |
| | | | 22.5 | 2 | 45 |
| | | | 48.3 | 5 | 39 |
| | | | 59.9 | 7 | 34 |
| | | | 70.2 | 9 | 31 |
| | | | 89.4 | 24 | 15 |
| 7[f] | 50 | 0.25 | 65 | 9 | 28 |
| 8[g] | 50 | 0.25 | 1.4 | 1 | 5.6 |
| | | | 2.2 | 4 | 2.2 |
| | | | 8.0 | 9 | 3.5 |
| | | | 33.6 | 24 | 5.6 |

[a] Catalysis conditions: diphenylacetylene (0.5 mmol, 89 mg), water (0.55 mmol, 9.9 μL) and γ-valerolactone (240 μL).[b] (mol of catalyst / mol of alkyne) x 100. [c] Determined by $^1$H NMR; average value of three measurements. [d] Time necessary to reach the reported conversion. [e] TOF = (mol product / mol catalyst)/t(h) at the

reported conversion. [f] ethyl lactate instead of GVL. [g] propylene carbonate instead of GVL.

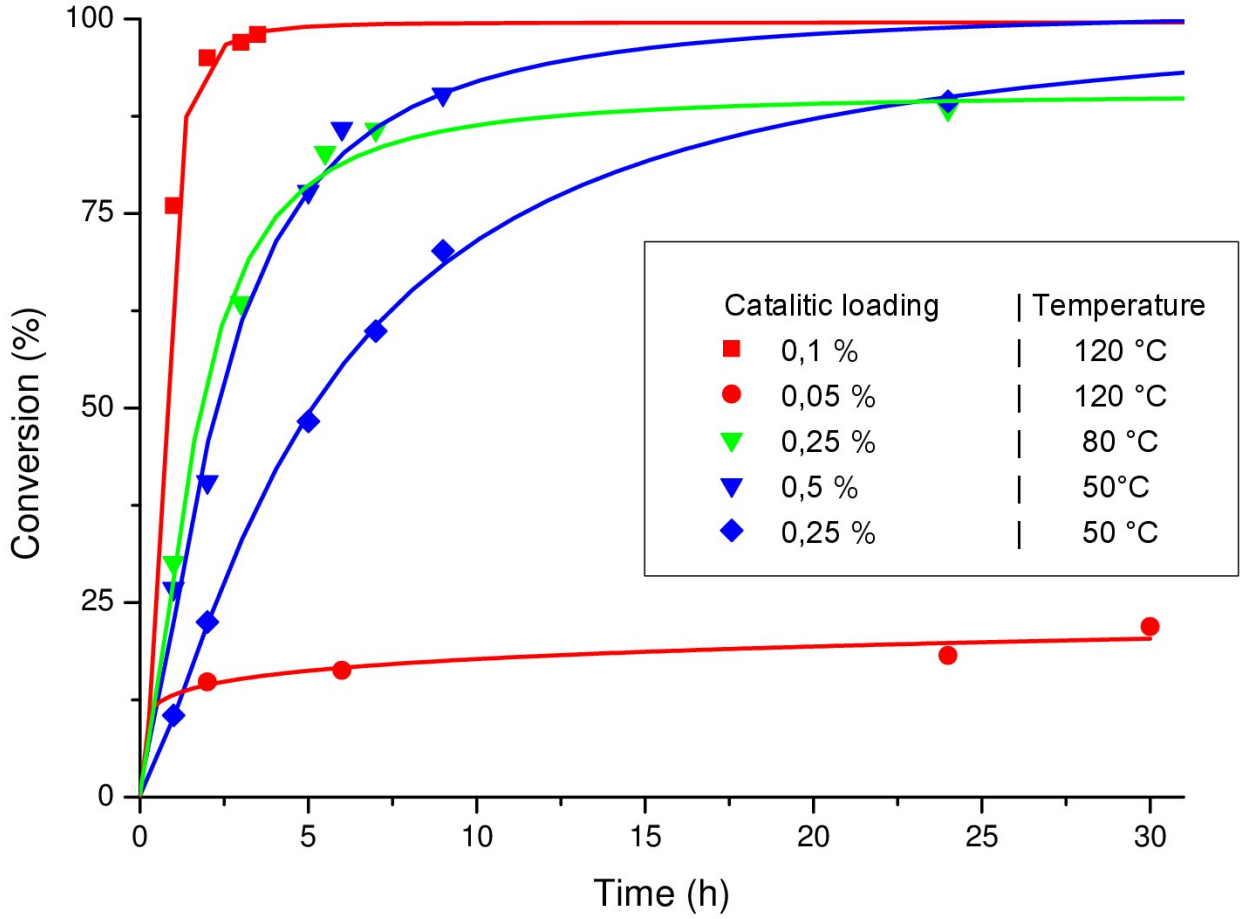



**Figure S1**. NHC-Au-OTf catalyzed hydration of diphenylacetylene in γ-valerolactone (Table S1)

**Table S2**: Hydration of alkynes in γ-valerolactone.[a]

| Entry | Substrate | Temp (°C) | Loading (mol %)[b] | Conv (%)[c] | Time (h)[d] | TOF[e] ($h^{-1}$) | I.R. ($\%_a$:$\%_b$)[f] |
|---|---|---|---|---|---|---|---|
| 1 | 3-phen-1-propyne | 120 | 0.1 | 96 | 0.5 | 1920 | - |
| | | | | >99 | 1 | 990 | |
| 2 | 1-phenyl-1-propyne | | | 50 | 0.5 | 1000 | 96:4 |
| | | | | 55 | 1 | 550 | 84:16 |
| | | | | 57 | 1.5 | 380 | 83:17 |
| | | | | 64[a] | 2.5 | 256 | 84:16 |
| 3 | 3-hexyne | 30 | | 24 | 2 | 120 | - |
| | | | | 84 | 5 | 168 | |
| | | | | 92 | 8 | 115 | |
| 4 | Phenylacetylene | 120 | 0.1 | 90.1 | 0.5 | 1802 | - |
| | | | | 94.9 | 1 | 949 | |
| | | | | 99.5 | 1.5 | 663 | |
| 5 | | | 0.05 | 46.5 | 16 | 58 | - |
| | | | | 65.9 | 42 | 31 | |
| | | | | 79.3 | 89 | 18 | |
| 6 | | | 0.01 | 0 | 89 | 0 | - |
| 7 | | | 0.005 | 0 | 89 | 0 | - |
| 8 | | 80 | 0.2 | 80.8 | 1 | 404 | - |
| | | | | 97.5 | 2 | 244 | |
| | | | | 98.9 | 5 | 99 | |
| | | | | 99.3 | 7 | 71 | |
| 9 | | | 0.1 | 10.8 | 1 | 108 | - |
| | | | | 17.1 | 2 | 86 | |
| | | | | 26.3 | 5 | 53 | |
| | | | | 23.8 | 7 | 34 | |
| 10 | | | 0.1 | 6.1 | 1 | 61 | - |
| | | | | 10.2 | 3 | 34 | |
| | | | | 10.9 | 5.5 | 20 | |
| | | | | 13.9 | 7 | 20 | |
| | | | | 16.6 | 24 | 7 | |
| 11 | | 50 | 0.5 | 45.4 | 1 | 91 | - |
| | | | | 92.7 | 2 | 93 | |
| | | | | 99.9 | 5 | 40 | |
| 12 | | | 0.25 | 13.8 | 1 | 55 | - |
| | | | | 25.7 | 2 | 51 | |
| | | | | 60.7 | 5 | 49 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | 69.5 | 7 | 40 | |
| | | | | 86.6 | 9 | 38 | |

[a] Catalysis conditions: see above. [b] (mol of catalyst / mol of alkyne) x 100. [c] Determined by $^{1}H$ NMR; average value of three measurements. [d] Time necessary to reach the reported conversion. [e] TOF = (mol product / mol catalyst)/t(h) at the reported conversion. [f]Isomeric ratio

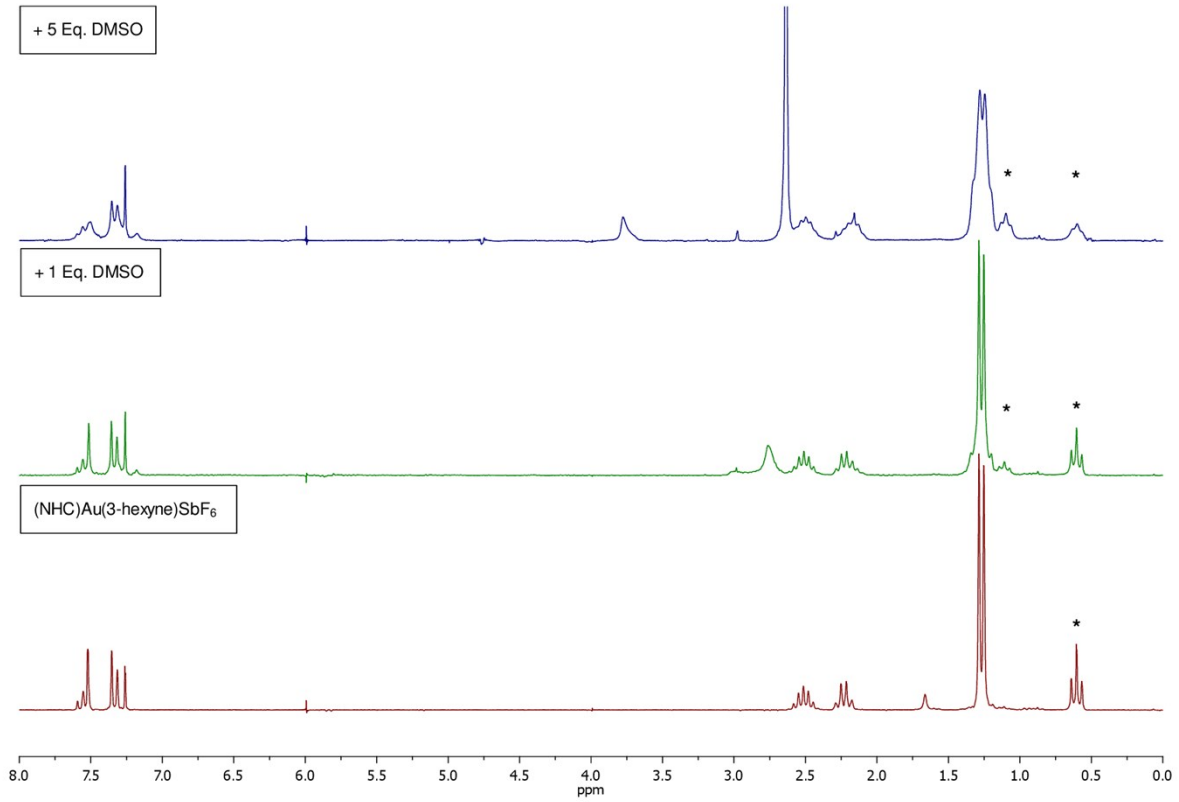



**Figure S2.** $^{1}H$ NMR spectra of NHC-Au-(3-hexyne)$SbF_6$ ($CDCl_3$) in presence of different equivalents of DMSO. (* denotes signal $CH_3$ of 3-hexyne)

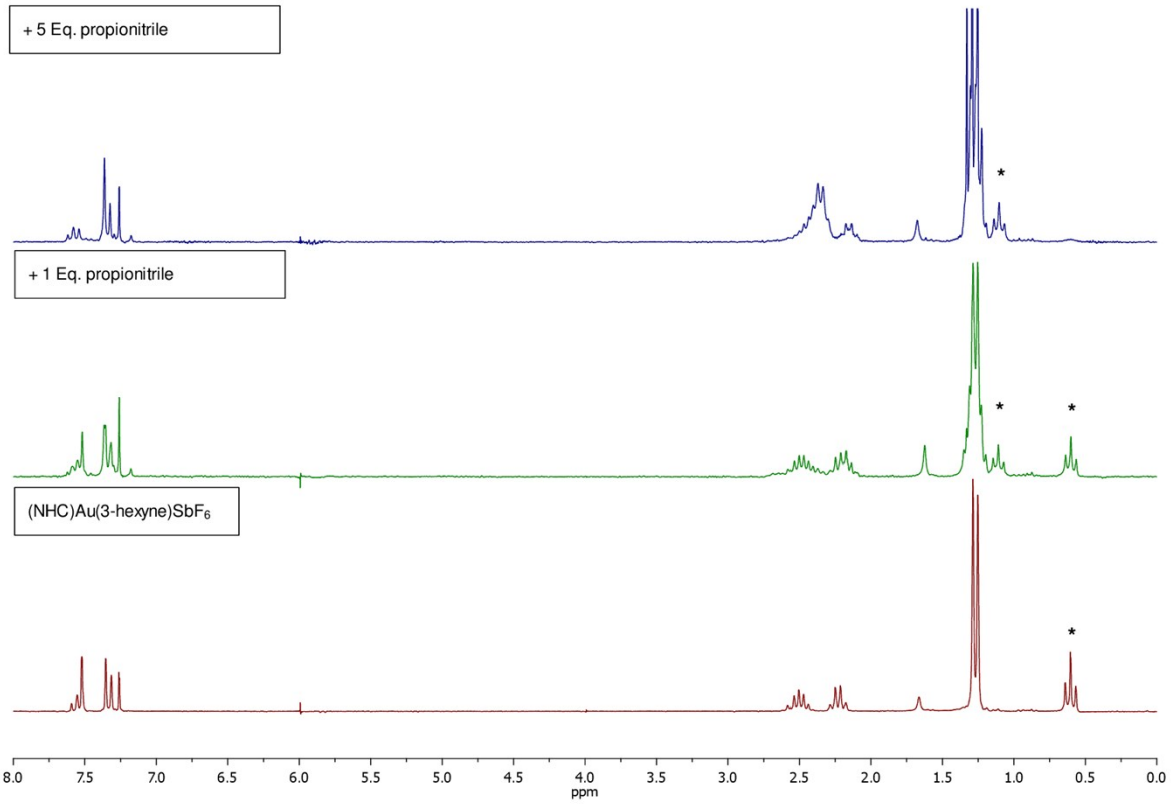



**Figure S3.** $^{1}H$ NMR spectra of NHC-Au-(3-hexyne)$SbF_6$ ($CDCl_3$) in presence of different equivalents of propionitrile. (* denotes signal $CH_3$ of 3-hexyne)

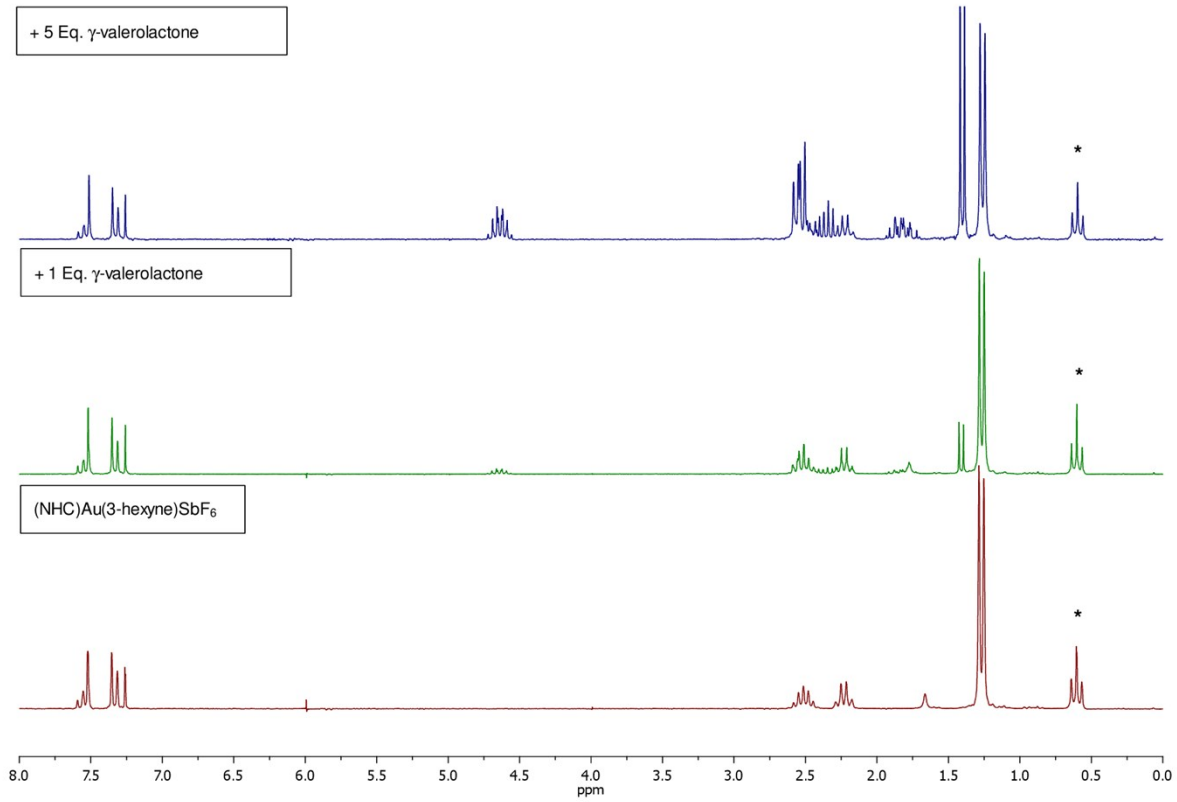



**Figure S4.** $^{1}H$ NMR spectra of NHC-Au-(3-hexyne)$SbF_6$ ($CDCl_3$) in presence of different equivalents of γ-valerolactone. (* denotes signal $CH_3$ of 3-hexyne)

## 4. COMPUTATIONAL DETAILS

Complex NHC'-Au-OTf (NHC' = 1,3-dimethylimidazol-2-ylidene; $OTf^-$ = Trifluoromethanesulfonate or triflate anion) and 2-butyne have been used as a model for the catalyst and substrate, respectively, in the calculations.The computational study has been performed with ADF2014.05 program package[7] to identify reactant complex, transition state and product complex structures of the nucleophilic attack step in the catalytic process for the carbene-gold(I) catalyzed addition of methanol to alkyne reaction, including one explicit solvent molecule, γ-valerolactone (GVL), nitromethane (NM) or chloroform (TCMA). The geometry optimization calculations have been carried out at the DFT level of theory using the GGA functional BP86.[8] All atoms have been described with a Slater-type TZ2P triple- ς quality basis set, using the frozen core approximation (core small). Relativistic effects have been included with the scalar zero-order regular approximation ZORA model.[9] Solvation effects have been taken into account by the Conductor like Screening Model COSMO[10] using nitromethane as solvent. Final energies have been calculated with ORCA package[11] by single point double-hybrid B2PLYP functional[12] calculations on the optimized BP86 solution phase structures with a Def2-TZVP basis set for all atoms and ECP for gold to account for relativistic effects. This computational protocol combining BP86 geometry optimizations and B2PLYP single-point energy calculations has been shown to give an high accuracy to describe gold species along reaction pathways in benchmark studies.[13] The reference energy has been set to the most stable adduct involving five molecules ($[NHC'\text{-}Au]^+$, 2-butyne, methanol, $OTf^-$ and one explicit solvent molecule) for activation energy barriers evaluation in order to minimize entropy problems. For such a kind of reactions the entropic contribution was found to be indeed small, as shown in the SI of our reference.[5] For this reason, computational mechanistic analysis is presented in enthalpy energies in this work. Frequency calculations at the same BP86 level of theory have been also performed to identify all stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency). Restricted calculations have been carried out for the closed shell singlet state.

## Solvent (GVL, NM)-assisted nucleophilic attack step for the addition of methanol to 2-butyne

The reactant complex RC_X(Y), where the anion (RC_OTf(GVL)) or the γ-valerolactone solvent (RC_GVL(OTf)), acts as a hydrogen-bond acceptor, enhancing the nucleophilicity of the attacking methanol, are the starting complex for this study (Figures S5 and S6).

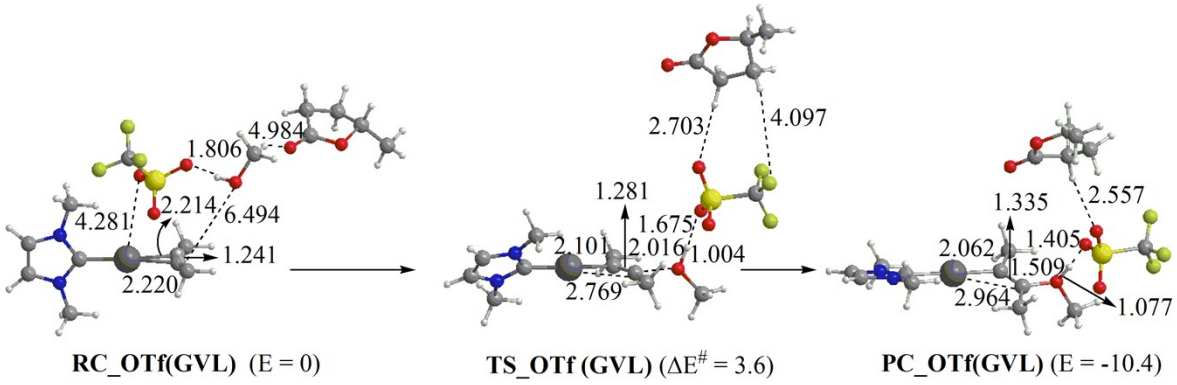



**Figure S5**. Reactant complex RC_OTf(GVL), transition state TS_OTf(GVL) and product complex PC_OTf(GVL) in the methanol nucleophilic attack for the addition of methanol to 2-butyne reaction assisted by $OTf^-$ anion. Energies values (kcal/mol) refer to RC_OTf(GVL) taken as zero. Bond lengths are in angstrom.

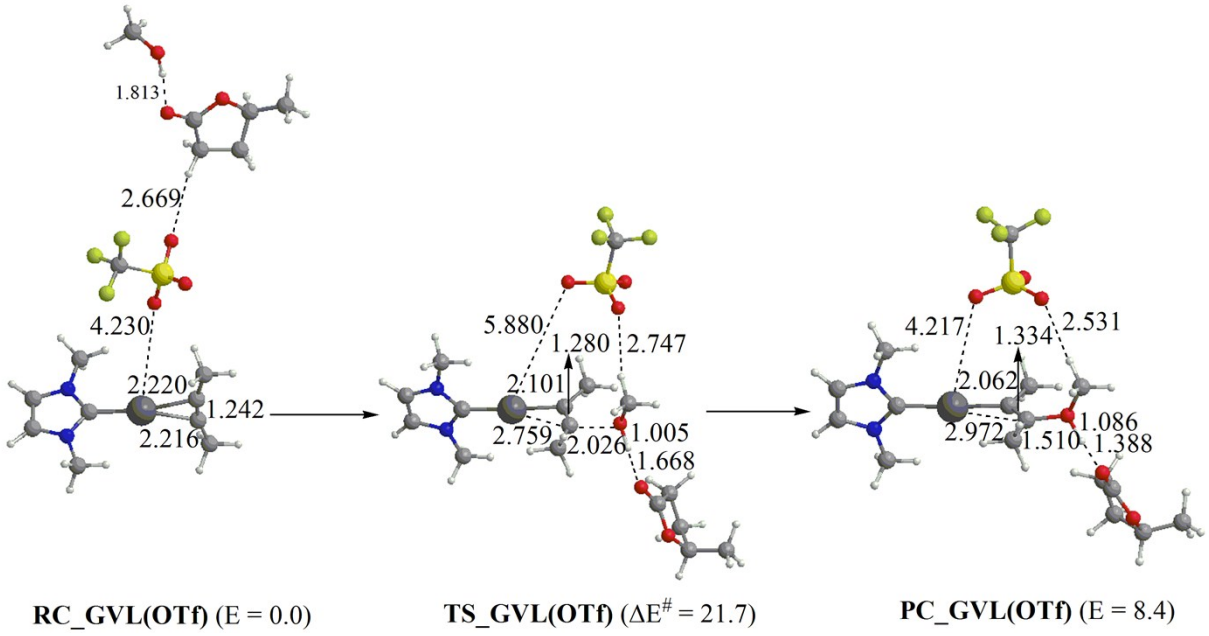



**Figure S6**. Reactant complex RC_GVL(OTf), transition state TS_GVL(OTf) and product complex PC_GVL(OTf) in the methanol nucleophilic attack for the addition of methanol to 2-butyne reaction assisted by solvent GVL molecule. Energies values (kcal/mol) refer to RC_GVL(OTf) taken as zero. Bond lengths are in angstrom.

Note that for the methanol attack to the butyne-coordinated species, [NHC'-Au-(2-butyne)]$^+$, any interaction between the anion and the solvent molecule is switched off both in RC_OTf(GVL) and RC_GVL(OTf). Interestingly, in the transition state TS_OTf(GVL) structure an anion-solvent interaction arises which moves the anion towards an outer position at the substrate side. Conversely, the characteristic template structure of RC_X(Y) with the anion in the bridging position between Au and methanol, weakly interacting with Au, is retained in TS_GVL(OTf). The activation barrier corresponding to the transition state structure involved in this process amounts to 3.6 kcal/mol for the anion-mediated and to 21.7 kcal/mol for the solvent-mediated nucleophilic attack to the substrate. The transition state TS_X(Y) evolves with the formation of the product complex of this step PC_X(Y), which is more stable than RC_X(Y) by 10.4 and less stable than RC_X(Y) by 8.4 kcal/mol for the anion-assisted (PC_OTf(GVL)) and solvent-assisted (PC_GVL(OTf)) process, respectively. This result suggests that the anion is able to activate the nucleophile much more efficiently than the solvent molecule thus ruling out the hypothesis that the better performance of the catalyst in GVL could be ascribed to GVL replacing the OTf$^-$ in

the activation of methanol. To verify if the solvent-anion interaction could enhance the efficiency of the solvent in the nucleophile activation, starting from RC_GVL(OTf) a transition state structure TS_GVL(OTf)' has been calculated (Figure S7).

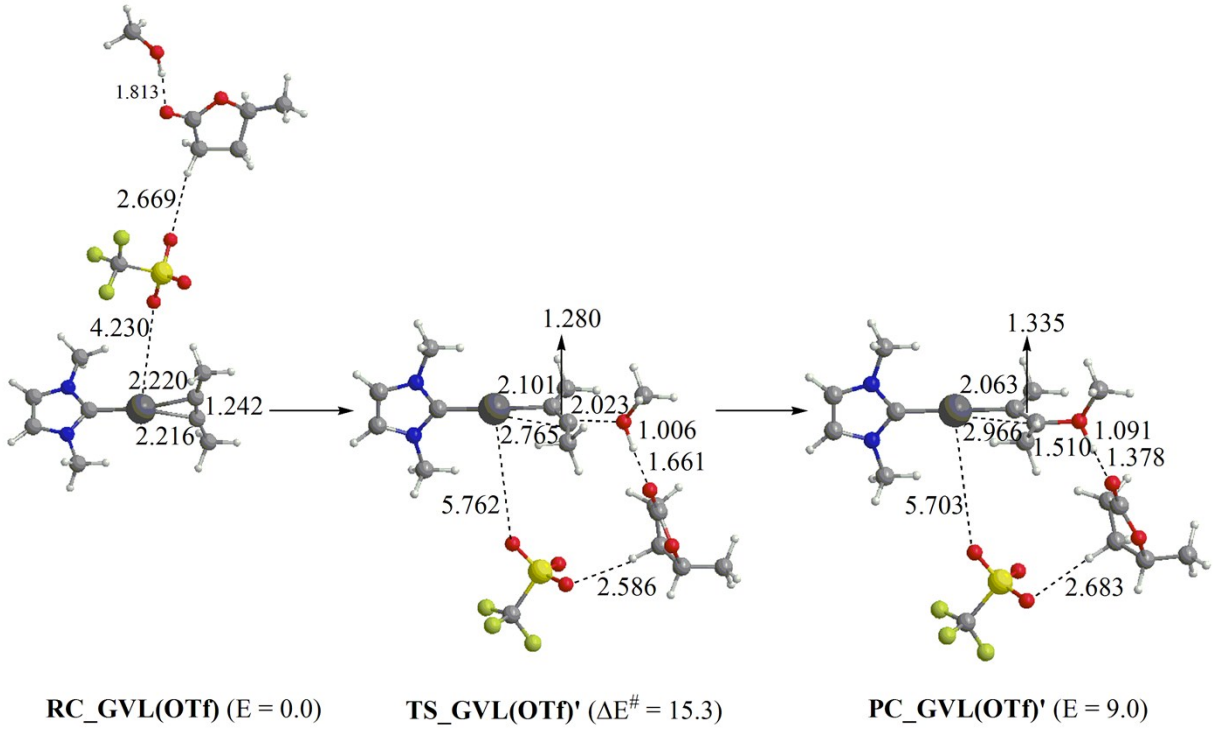



**Figure S7**. Reactant complex RC_GVL(OTf), transition state TS_GVL(OTf)' and product complex PC_GVL(OTf)' in the methanol nucleophilic attack for the addition of methanol to 2-butyne reaction assisted by a solvent GVL molecule interacting with $OTf^-$ anion. Energies values (kcal/mol) refer to RC_GVL(OTf) taken as zero. Bond lengths are in angstrom.

The activation energy barrier is decreased with respect to that calculated with TS_GVL(OTf) (15.3 vs. 21.7 kcal/mol, respectively) but it is still larger than that calculated with TS_OTf(GVL) (3.6 kcal/mol). This finding further corroborates the result that the $OTf^-$ anion is the crucial species in the nucleophilic activation of methanol in γ-valerolactone as solvent.

Corresponding calculations have been performed by replacing the γ-valerolactone molecule with the nitromethane molecule. Similar results are obtained which show that $OTf^-$ rather than the solvent is involved in the nucleophilic activation of methanol in nitromethane as well. The activation barrier amounts to 6.4 kcal/mol for the anion-

mediated (Figure S8) and to 33.9 kcal/mol for the solvent-mediated (Figure S9) nucleophilic attack to the substrate. Analogously, the solvent-anion interaction enhances the efficiency of the solvent in the nucleophile activation (the calculated activation energy barrier is 18.8 kcal/mol, Figure S10). Note that the activation energy barrier for the anion-assisted nucleophilic attack is larger in nitromethane (6.4 kcal/mol) than in γ-valerolactone (3.6 kcal/mol), in nice agreement with experiment.

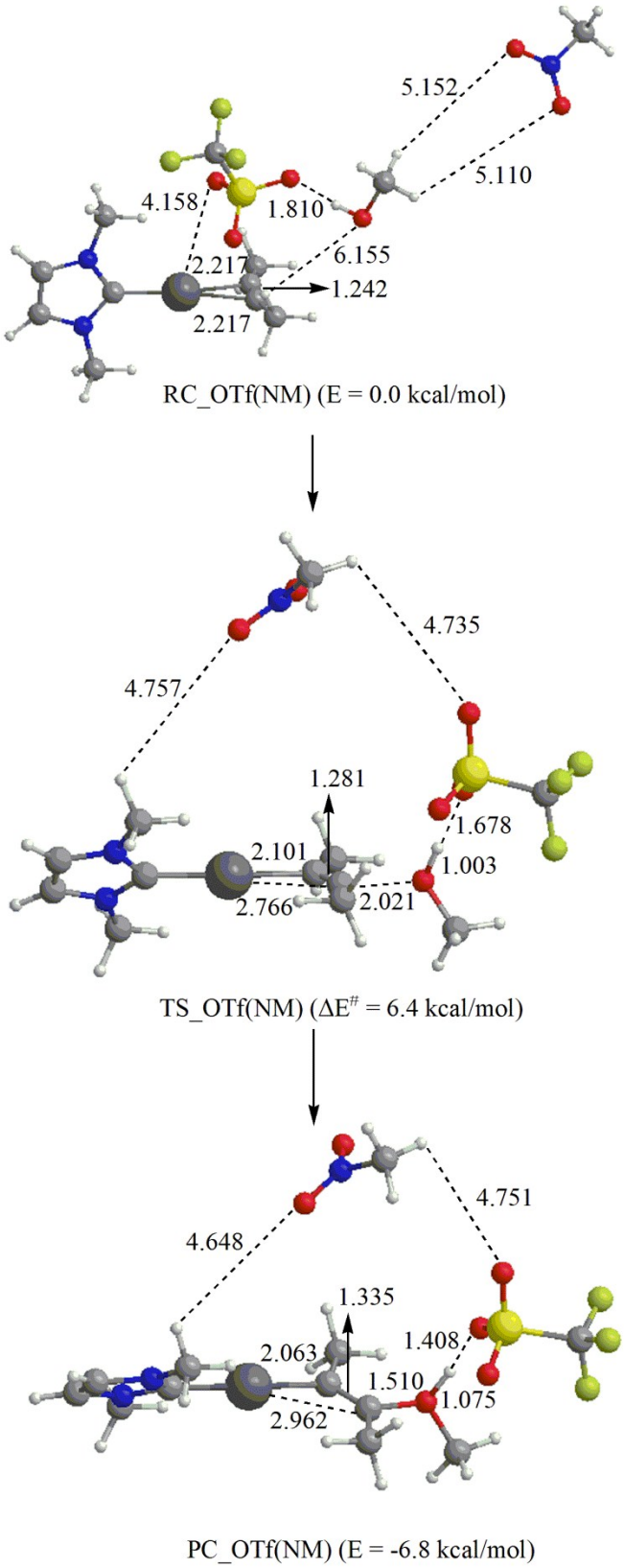



**Figure S8**. Reactant complex RC_OTf(NM), transition state TS_OTf(NM) and product complex PC_OTf(NM) in the methanol nucleophilic attack (RDS) for the addition of methanol to 2-butyne reaction assisted by $OTf^-$ anion. Energies values (kcal/mol) refer to RC_OTf(NM) taken as zero. Bond lengths are in angstrom.

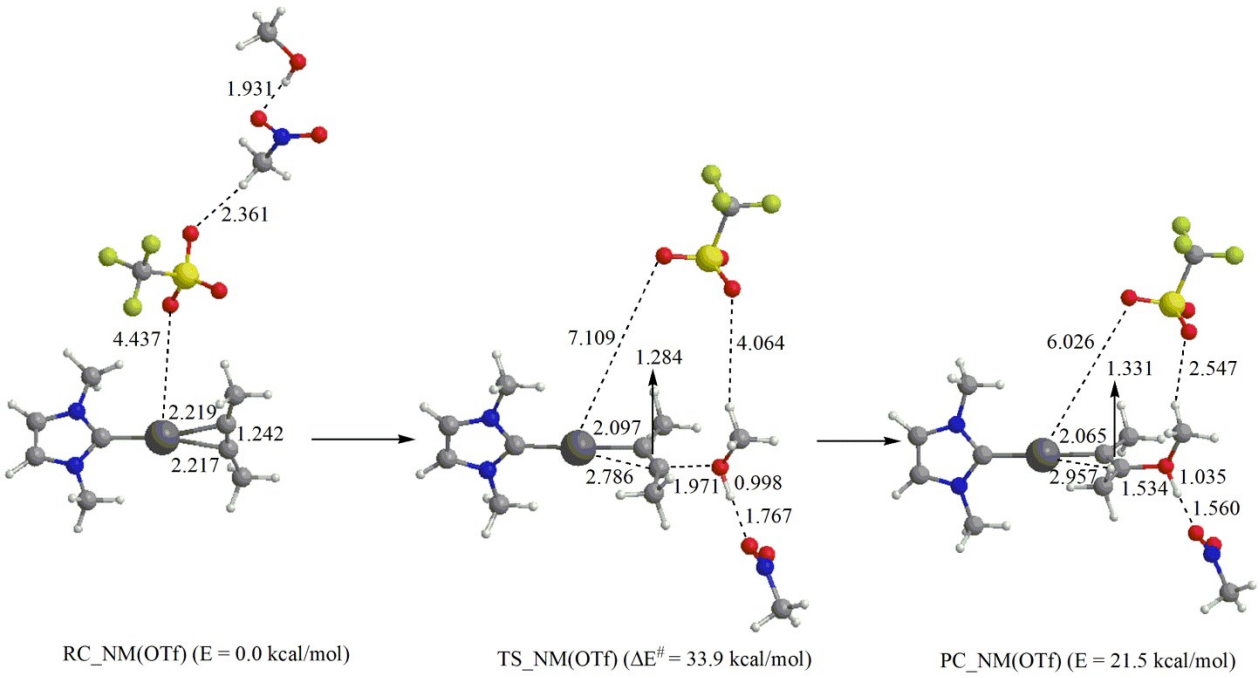



**Figure S9**. Reactant complex RC_NM(OTf), transition state TS_NM(OTf) and product complex PC_NM(OTf) in the methanol nucleophilic attack (RDS) for the addition of methanol to 2-butyne reaction assisted by a solvent NM molecule. Energies values (kcal/mol) refer to RC_NM(OTf) taken as zero. Bond lengths are in angstrom.

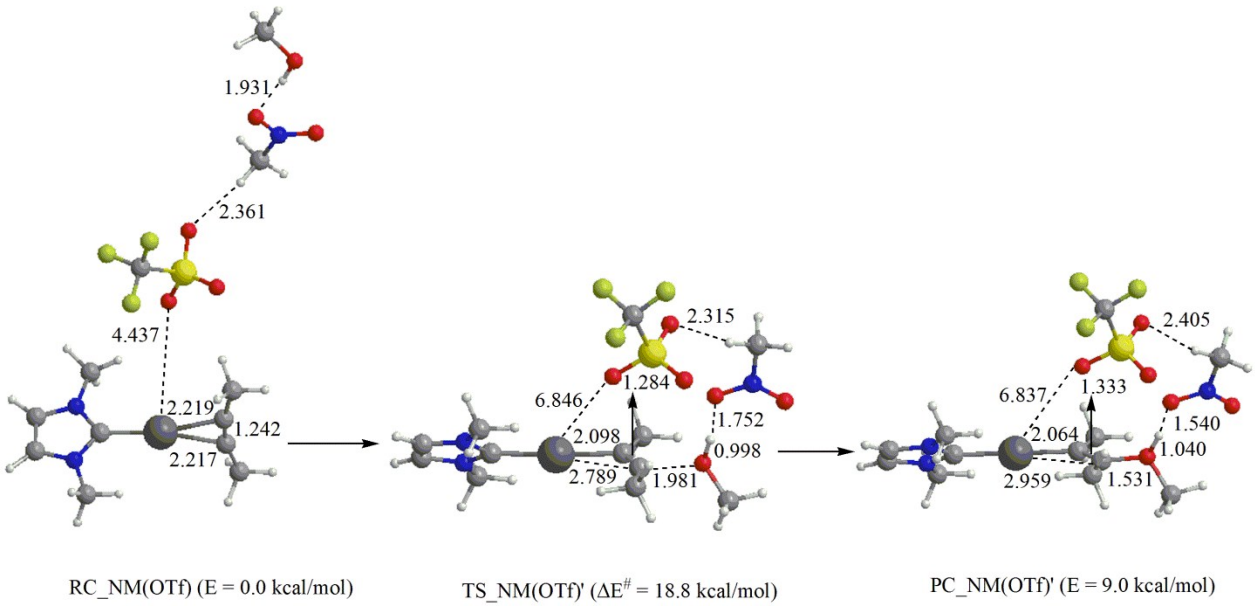



**Figure S10**. Reactant complex RC_NM(OTf), transition state TS_NM(OTf)' and product complex PC_NM(OTf)' in the methanol nucleophilic attack (RDS) for the addition of methanol to 2-butyne reaction assisted by a solvent NM molecule interacting with $OTf^-$ anion. Energies values (kcal/mol) refer to RC_NM(OTf) taken as zero. Bond lengths are in angstrom.

## Solvent-anion interaction in the nucleophilic attack step for the addition of methanol to 2-butyne: ion pairs

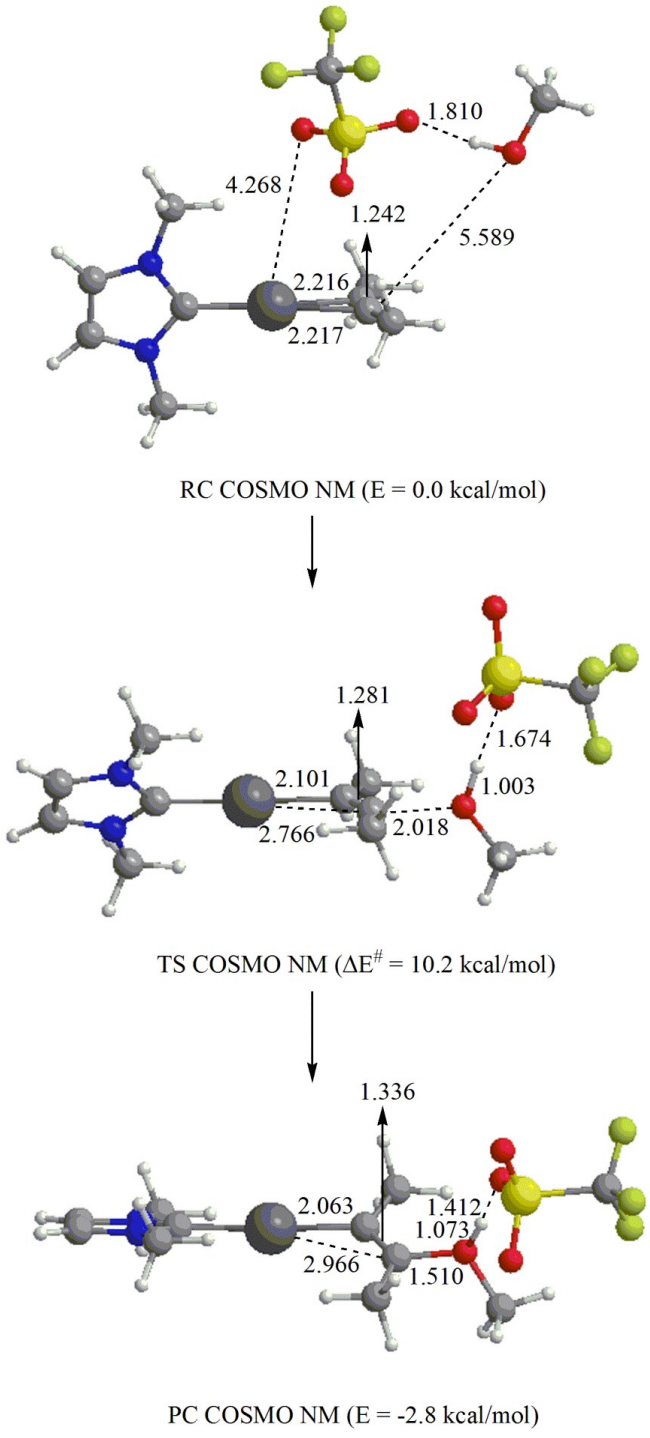



**Figure S11**. Reactant complex RC COSMO NM, transition state TS COSMO NM and product complex PC COSMO NM in the methanol nucleophilic attack (RDS) for the addition of methanol to 2-butyne reaction assisted by $OTf^-$ anion including only implicit COSMO solvent NM. Energies values (kcal/mol) refer to RC COSMO NM taken as zero. Bond lengths are in angstrom.

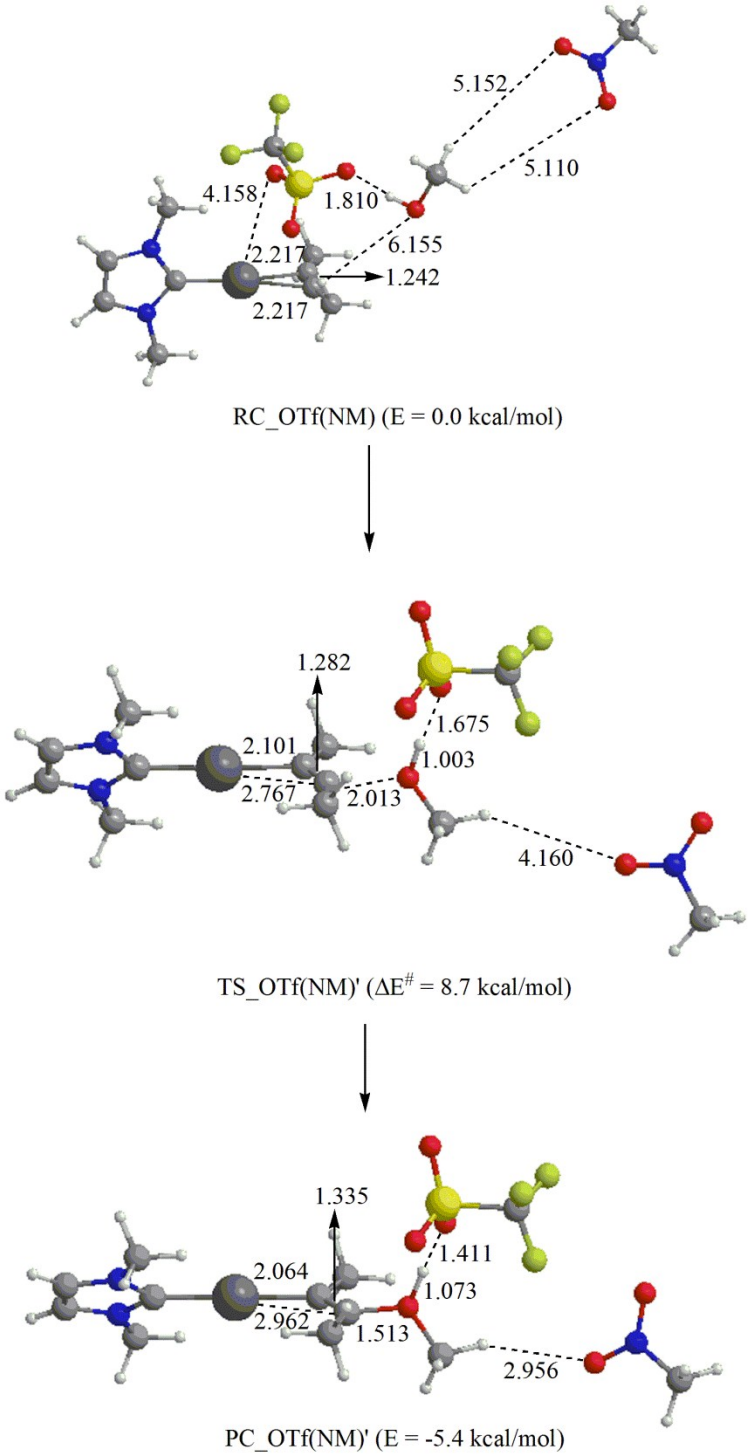
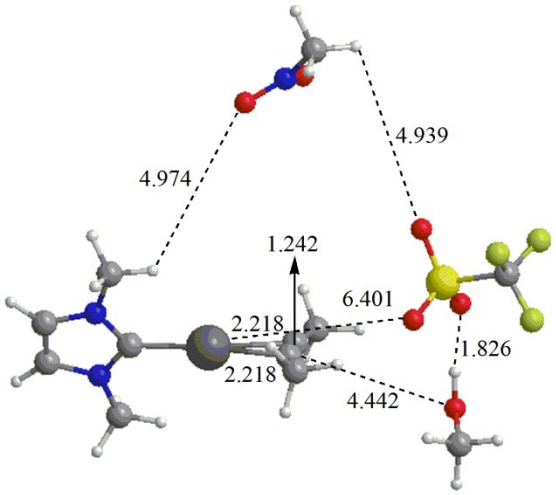
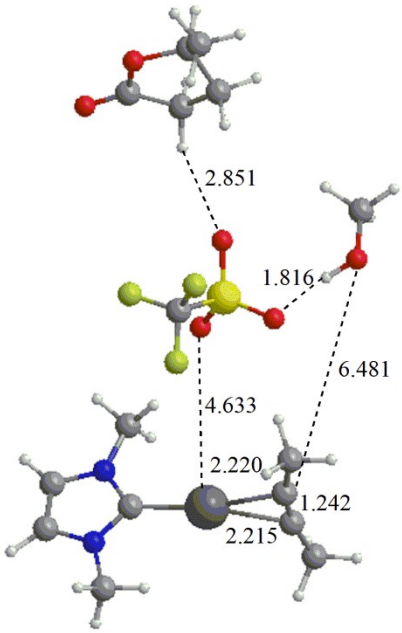



**Figure S12**. Reactant complex RC_OTf(NM), transition state TS_OTf(NM)' and product complex PC_OTf(NM)' in the methanol nucleophilic attack (RDS) for the addition of methanol to 2-butyne reaction assisted by $OTf^-$ anion in the presence of an explicit NM solvent molecule interacting with methanol. Energies values (kcal/mol) refer to RC_OTf(NM) taken as zero. Bond lengths are in angstrom.



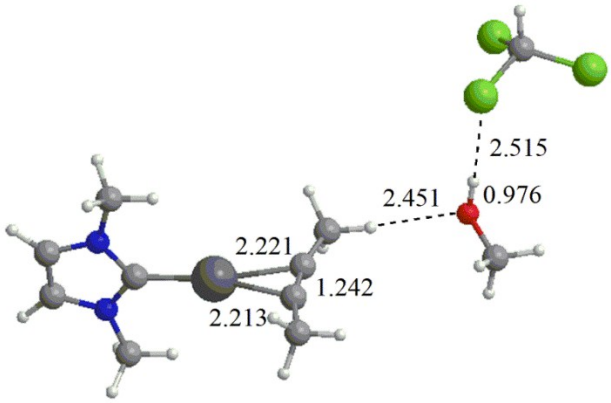

RC'_OTf(NM)



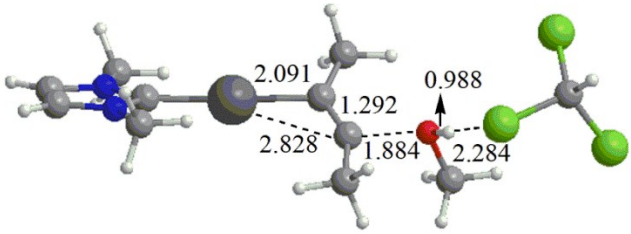

RC'_OTf(GVL)

**Figure S13**. Reactant complexes RC'_OTf(NM) and RC'_OTf(GVL) optimized geometrical structures. Bond lengths are in angstrom.

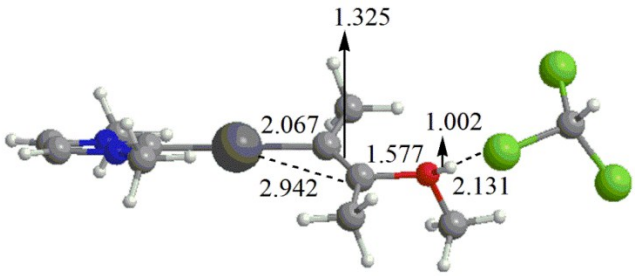
**Solvent-nucleophile interaction in the nucleophilic attack step for the addition of methanol to 2-butyne: free ions**




[RC_TCMA]$^+$

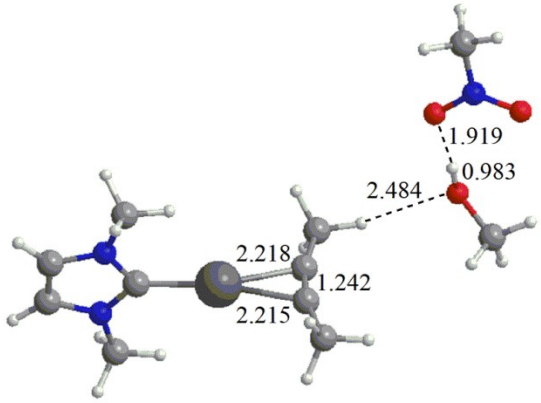



[TS_TCMA]$^+$

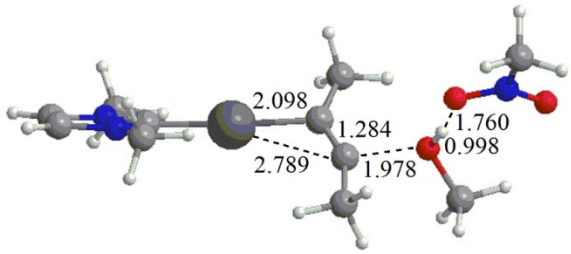



[PC_TCMA]$^+$

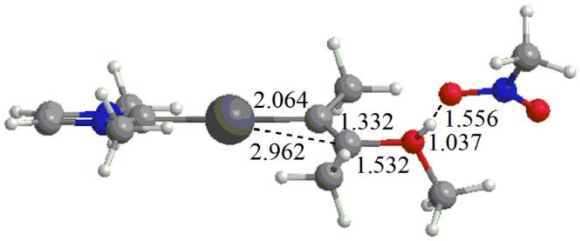
**Figure S14**. Reactant complex [RC_TCMA]$^+$, transition state [TS_TCMA]$^+$ and product complex [PC_TCMA]$^+$ in the methanol nucleophilic attack (RDS) for the addition of methanol to 2-butyne reaction assisted by an explicit TCMA solvent molecule interacting with methanol in the absence of the anion. Bond lengths are in angstrom.




$[RC\_NM]^+$

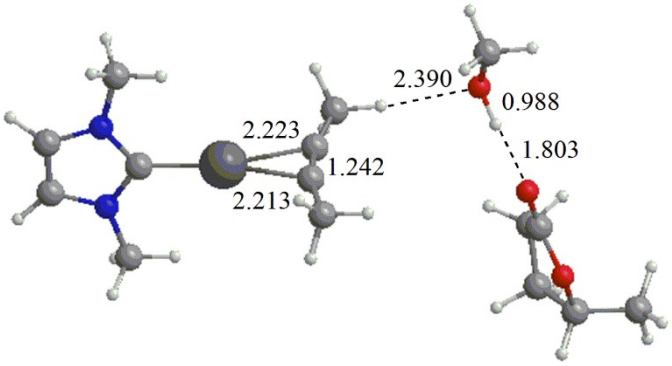



$[TS\_NM]^+$

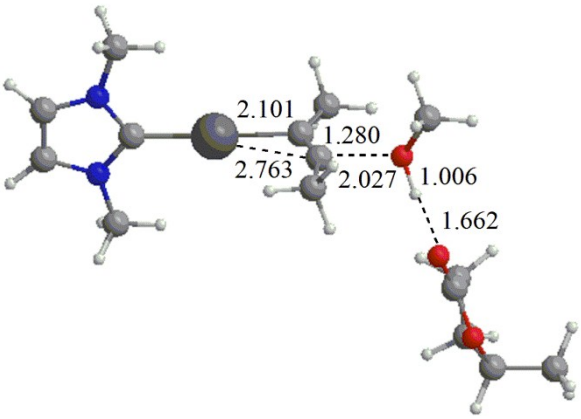



$[PC\_NM]^+$

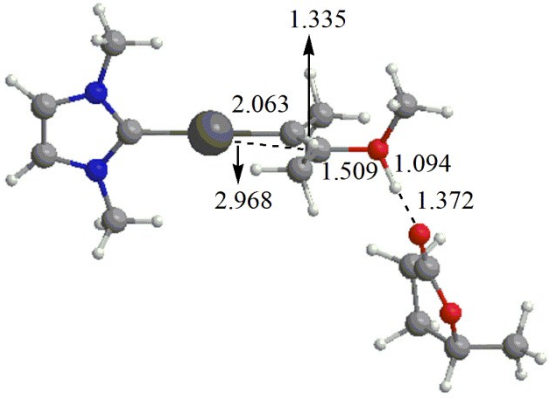
**Figure S15**. Reactant complex $[RC\_NM]^+$, transition state $[TS\_NM]^+$ and product complex $[PC\_NM]^+$ in the methanol nucleophilic attack (RDS) for the addition of methanol to 2-butyne reaction assisted by an explicit NM solvent molecule interacting with methanol in the absence of the anion. Bond lengths are in angstrom.




$[RC\_GVL]^+$




$[TS\_GVL]^+$




$[PC\_GVL]^+$

**Figure S16**. Reactant complex $[RC\_GVL]^+$, transition state $[TS\_GVL]^+$ and product complex $[PC\_GVL]^+$ in the methanol nucleophilic attack (RDS) for the addition of methanol to 2-butyne reaction assisted by an explicit GVL solvent molecule interacting with methanol in the absence of the anion. Bond lengths are in angstrom.

## REFERENCES


[1] L. Hintermann, *Beilstein Journal of Organic Chemistry*, 2007, **22**, 1.

[2] R. Uson, A. Laguna and M. Laguna, *Inorg. Syn.*, 1989, **26**, 85.

[3] A. Collado, A. Gómez-Suárez, A. R. Martin, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun*., 2013, **49**, 5541.

[4] D. Gasperini, A. Collado, A. Goméz-Suárez, D. B. Cordes, A. M. Z. Slawin and S. P. Nolan, *Chem. Eur. J.*, 2015, **21**, 5403.

[5] L. Biasiolo, M. Trinchillo, P. Belanzoni, L. Belpassi, V. Busico, G. Ciancaleoni, A. D'Amora, A. Macchioni, F. Tarantelli and D. Zuccaccia, *Chem. Eur. J.*, 2014, **20**, 14594.

[6] M. Gatto, P. Belanzoni, L. Belpassi, L. Biasiolo, A. Del Zotto, F. Tarantelli and D. Zuccaccia, *ACS Catal*., 2016, **6**, 7363.

[7] a) E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41; b) G. Te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra and S. J. A. van Gisbergen, *J. Comput. Chem*, 2001, **22**, 931; c) ADF2014.05, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, 2014, http://www.scm.com.

[8] a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; b) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.

[9] a) E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, **101**, 9783; b) E. van Lenthe, R. van Leeuwen and E. J. Baerends, *Int. J. Quantum Chem.*, 1996, **57**, 281.

[10] a) A. Klamt and G. J. Schüürmann, *Chem. Soc. Perkin Trans.*¸1993, **2**, 799; b) A. J. Klamt, *Phys. Chem.*, 1995, **99**, 2224; c) A. Klamt and V. J. Jones, *Chem. Phys.*, ***1996***, **105**, 9972.

[11] F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73.

[12] S. Grimme, *J. Chem. Phys.*, 2006, **124**, 034108.

[13] G. Ciancaleoni, S. Rampino, D. Zuccaccia, F. Tarantelli, P. Belanzoni and L. Belpassi, *J. Chem. Theory Comput*., 2014, **10**, 1021.

**Optimized structures xyz coordinates**

**RC_OTf(GVL)**

55

| | | | |
|---|---|---|---|
| C | -2.096676 | 2.709450 | -1.845908 |
| N | -2.796370 | 3.802367 | -2.313031 |
| C | -4.095210 | 3.471768 | -2.546564 |
| N | -4.194391 | 2.154039 | -2.220964 |
| C | -2.977526 | 1.670482 | -1.787924 |
| C | -2.210077 | 5.129773 | -2.494967 |
| Au | -5.571797 | 4.686976 | -3.199831 |
| C | -6.944764 | 5.890567 | -4.463365 |
| C | -6.765258 | 5.937964 | -5.915171 |
| C | -5.411077 | 1.348413 | -2.304681 |
| C | -7.317013 | 6.045578 | -3.289311 |
| C | -8.016296 | 6.446661 | -2.065792 |
| O | -3.073943 | 7.969420 | -4.346159 |
| S | -3.053589 | 8.259767 | -5.784135 |
| O | -3.487511 | 7.166986 | -6.666475 |
| O | -3.586434 | 9.591724 | -6.143910 |
| C | -1.214514 | 8.425294 | -6.171521 |
| F | -0.559101 | 7.274572 | -5.890133 |
| F | -0.655190 | 9.416191 | -5.435386 |
| F | -1.017161 | 8.712645 | -7.479788 |
| O | -4.689509 | 10.372053 | -8.586085 |
| C | -4.589918 | 11.803513 | -8.576651 |
| H | -5.178786 | 12.248110 | -7.758451 |
| H | -4.987275 | 12.170533 | -9.529607 |
| H | -4.309949 | 10.045347 | -7.734889 |
| H | -2.840381 | 0.641058 | -1.484953 |
| H | -1.043616 | 2.759855 | -1.603937 |
| H | -5.777832 | 6.342485 | -6.176215 |
| H | -7.540046 | 6.587449 | -6.346036 |
| H | -6.862604 | 4.940337 | -6.361205 |
| H | -8.433292 | 5.577818 | -1.542143 |
| H | -8.842784 | 7.119247 | -2.333623 |
| H | -7.345099 | 6.973816 | -1.376564 |
| H | -5.716485 | 1.031033 | -1.302439 |
| H | -5.226396 | 0.469231 | -2.929913 |
| H | -6.199530 | 1.958646 | -2.753213 |
| H | -2.886959 | 5.743767 | -3.096714 |
| H | -1.252025 | 5.028951 | -3.013905 |
| H | -2.049277 | 5.602476 | -1.519363 |
| H | -3.545284 | 12.139199 | -8.482179 |
| O | -8.234309 | 12.545561 | -3.832338 |
| C | -8.913527 | 13.421592 | -3.323296 |
| C | -8.716788 | 14.126934 | -1.997018 |

| | | | |
|---|---|---|---|
| C | -10.070211 | 14.792796 | -1.740862 |
| C | -10.622058 | 15.008162 | -3.155175 |
| O | -10.016543 | 13.908567 | -3.949680 |
| H | -7.909648 | 14.862859 | -2.130569 |
| H | -8.393911 | 13.416096 | -1.229257 |
| H | -9.997234 | 15.736002 | -1.190050 |
| H | -10.732009 | 14.115687 | -1.184117 |
| H | -10.226228 | 15.935996 | -3.591849 |
| C | -12.125374 | 14.947581 | -3.300404 |
| H | -12.573564 | 15.776091 | -2.736948 |
| H | -12.428419 | 15.047490 | -4.349803 |
| H | -12.519199 | 14.004068 | -2.900356 |

**TS_OTf(GVL)**

55

| | | | |
|---|---|---|---|
| C | -5.572973 | -0.582407 | -3.193927 |
| N | -5.344389 | 0.769380 | -3.373836 |
| C | -6.352972 | 1.337634 | -4.090806 |
| N | -7.216095 | 0.317996 | -4.352649 |
| C | -6.753864 | -0.866603 | -3.809217 |
| C | -4.163890 | 1.471338 | -2.876308 |
| Au | -6.544263 | 3.286351 | -4.630005 |
| C | -6.895758 | 5.300148 | -5.113802 |
| C | -5.809515 | 5.772006 | -5.603264 |
| O | -6.106289 | 7.731798 | -5.973729 |
| C | -5.625168 | 8.278287 | -7.220969 |
| C | -8.472280 | 0.445454 | -5.087477 |
| C | -8.247796 | 5.881628 | -4.836224 |
| C | -4.419557 | 5.643597 | -6.041115 |
| O | -5.034512 | 9.009289 | -3.882156 |
| S | -3.603134 | 9.078454 | -3.490537 |
| O | -2.691678 | 8.373238 | -4.400438 |
| O | -3.368713 | 8.870479 | -2.057388 |
| C | -3.191712 | 10.899522 | -3.753506 |
| F | -1.898363 | 11.139164 | -3.441531 |
| F | -3.969207 | 11.681597 | -2.970945 |
| F | -3.392237 | 11.254327 | -5.042252 |
| H | -5.923480 | 9.332312 | -7.286829 |
| H | -6.099828 | 7.715922 | -8.030249 |
| H | -5.639587 | 8.193798 | -5.214816 |
| H | -7.297930 | -1.796952 | -3.904223 |
| H | -4.884229 | -1.216877 | -2.652293 |
| H | -3.759162 | 6.333968 | -5.499112 |
| H | -4.315620 | 5.825442 | -7.118935 |
| H | -4.085196 | 4.616581 | -5.845923 |
| H | -9.026234 | 5.301972 | -5.349099 |
| H | -8.302993 | 6.925312 | -5.164353 |

| | | | |
|---|---|---|---|
| H | -8.472185 | 5.830515 | -3.762544 |
| H | -9.318437 | 0.252375 | -4.419131 |
| H | -8.488255 | -0.267690 | -5.918093 |
| H | -8.538554 | 1.464449 | -5.478862 |
| H | -4.291684 | 2.539558 | -3.072315 |
| H | -3.267011 | 1.106758 | -3.388855 |
| H | -4.063792 | 1.306979 | -1.798605 |
| H | -4.533488 | 8.200692 | -7.305015 |
| O | -2.279789 | 8.388335 | 2.431012 |
| C | -1.971804 | 9.555301 | 2.249440 |
| C | -2.536110 | 10.540940 | 1.248494 |
| C | -1.496386 | 11.663564 | 1.228230 |
| C | -0.876762 | 11.584328 | 2.628488 |
| O | -1.010657 | 10.150904 | 2.999655 |
| C | 0.575685 | 11.985963 | 2.741462 |
| H | -1.490233 | 12.131621 | 3.357894 |
| H | -0.726541 | 11.461771 | 0.470846 |
| H | -1.922224 | 12.653461 | 1.034112 |
| H | -2.718612 | 10.052092 | 0.285687 |
| H | -3.507082 | 10.882152 | 1.638526 |
| H | 0.948182 | 11.848767 | 3.763814 |
| H | 1.197491 | 11.401966 | 2.050212 |
| H | 0.674757 | 13.048535 | 2.482954 |

**PC_OTf(GVL)**

55

| | | | |
|---|---|---|---|
| C | -5.253729 | -0.023997 | -2.509033 |
| N | -4.985663 | 1.267502 | -2.925694 |
| C | -6.090569 | 1.843240 | -3.480164 |
| N | -7.053584 | 0.880841 | -3.399369 |
| C | -6.559718 | -0.267884 | -2.807645 |
| C | -3.683770 | 1.914814 | -2.792369 |
| Au | -6.267265 | 3.737576 | -4.244246 |
| C | -6.492822 | 5.653484 | -4.973182 |
| C | -5.443253 | 6.297230 | -5.490412 |
| O | -5.671564 | 7.723505 | -5.926897 |
| C | -5.397357 | 8.054020 | -7.331718 |
| C | -8.429176 | 1.033383 | -3.865709 |
| C | -7.862005 | 6.283876 | -4.864764 |
| C | -4.023474 | 5.889751 | -5.698274 |
| O | -4.770718 | 9.369879 | -4.310527 |
| S | -3.355561 | 9.877756 | -4.301452 |
| O | -2.527390 | 9.303344 | -5.364001 |
| O | -2.780803 | 9.944755 | -2.962466 |
| C | -3.583633 | 11.681330 | -4.803462 |
| F | -2.383339 | 12.298387 | -4.837599 |
| F | -4.373017 | 12.326397 | -3.919717 |

| | | | |
|---|---|---|---|
| F | -4.146611 | 11.766666 | -6.027368 |
| H | -5.750351 | 9.077535 | -7.475561 |
| H | -5.975410 | 7.356121 | -7.940327 |
| H | -5.209443 | 8.427254 | -5.255512 |
| H | -7.170940 | -1.146747 | -2.650792 |
| H | -4.503749 | -0.647749 | -2.041107 |
| H | -3.323898 | 6.570345 | -5.190174 |
| H | -3.745284 | 5.864743 | -6.762833 |
| H | -3.886689 | 4.881616 | -5.292845 |
| H | -8.613476 | 5.644474 | -5.350259 |
| H | -7.926188 | 7.287684 | -5.304586 |
| H | -8.162834 | 6.352803 | -3.808676 |
| H | -9.123994 | 0.922407 | -3.025850 |
| H | -8.651186 | 0.278623 | -4.627967 |
| H | -8.532264 | 2.032459 | -4.298559 |
| H | -3.780234 | 2.945957 | -3.144350 |
| H | -2.938178 | 1.387437 | -3.397543 |
| H | -3.372910 | 1.911646 | -1.742231 |
| H | -4.326795 | 7.973791 | -7.540178 |
| O | -3.096135 | 7.402169 | 1.043028 |
| C | -2.687922 | 8.523126 | 1.296232 |
| C | -3.058057 | 9.838175 | 0.643772 |
| C | -1.953396 | 10.791173 | 1.106134 |
| C | -1.511788 | 10.185852 | 2.444129 |
| O | -1.783670 | 8.733213 | 2.288113 |
| C | -0.059463 | 10.375458 | 2.817192 |
| H | -2.169655 | 10.518066 | 3.259766 |
| H | -1.113041 | 10.777373 | 0.398124 |
| H | -2.287918 | 11.827065 | 1.224691 |
| H | -3.145013 | 9.721286 | -0.441873 |
| H | -4.045971 | 10.128867 | 1.031252 |
| H | 0.179407 | 9.865137 | 3.757959 |
| H | 0.599962 | 9.997448 | 2.025149 |
| H | 0.139386 | 11.446825 | 2.951242 |

**RC_GVL(OTf)**

55

| | | | |
|---|---|---|---|
| O | -1.033366 | 1.992673 | -4.449102 |
| C | -1.736811 | 3.062382 | -4.870833 |
| C | -2.993137 | 3.230404 | -4.048069 |
| C | -2.726763 | 2.359970 | -2.817252 |
| C | -1.762294 | 1.295451 | -3.351388 |
| O | -1.350069 | 3.748371 | -5.810257 |
| C | -0.755624 | 0.745641 | -2.368571 |
| O | 0.877854 | 3.156930 | -7.398438 |
| C | 0.370045 | 2.727274 | -8.669915 |
| O | -4.659608 | 6.302342 | -2.888008 |

| | | | |
|---|---|---|---|
| S | -4.763143 | 7.680178 | -2.380700 |
| C | -4.358634 | 8.722474 | -3.898489 |
| F | -3.117627 | 8.437975 | -4.362117 |
| O | -6.123153 | 8.115708 | -2.026298 |
| O | -3.715028 | 8.069728 | -1.421047 |
| F | -4.405190 | 10.044986 | -3.610391 |
| F | -5.242926 | 8.480864 | -4.898090 |
| C | -8.505337 | 10.656269 | -3.118660 |
| N | -8.474034 | 12.081624 | -2.789613 |
| C | -8.896413 | 13.083213 | -3.638792 |
| C | -8.753289 | 14.260126 | -2.964694 |
| N | -8.248968 | 13.948113 | -1.719356 |
| C | -8.075161 | 12.604111 | -1.598167 |
| Au | -7.413171 | 11.587447 | 0.016943 |
| C | -7.300472 | 10.522806 | 1.956946 |
| C | -8.492351 | 10.367853 | 2.794635 |
| C | -7.944452 | 14.938553 | -0.688308 |
| C | -6.153620 | 10.494969 | 1.482066 |
| C | -4.732637 | 10.267709 | 1.214735 |
| H | -0.204132 | 1.790952 | -8.585397 |
| H | 1.229873 | 2.548790 | -9.326099 |
| H | -8.958184 | 15.278780 | -3.265004 |
| H | -9.251605 | 12.878885 | -4.639928 |
| H | -4.591243 | 9.651780 | 0.316218 |
| H | -4.293461 | 9.740528 | 2.073183 |
| H | -4.196192 | 11.214831 | 1.079021 |
| H | -8.899965 | 11.341695 | 3.091852 |
| H | -8.217606 | 9.812973 | 3.702164 |
| H | -9.277702 | 9.810318 | 2.269847 |
| H | -8.860186 | 15.464820 | -0.400310 |
| H | -7.211425 | 15.655391 | -1.071784 |
| H | -7.530915 | 14.417352 | 0.179371 |
| H | -7.758512 | 10.131119 | -2.515625 |
| H | -8.268917 | 10.534441 | -4.179447 |
| H | -9.501003 | 10.245923 | -2.917944 |
| H | -0.270030 | 3.494152 | -9.134271 |
| H | -3.831348 | 2.848665 | -4.651175 |
| H | -3.190845 | 4.287232 | -3.839860 |
| H | -3.631073 | 1.907598 | -2.397412 |
| H | -2.233710 | 2.947074 | -2.030661 |
| H | -2.311540 | 0.481501 | -3.844636 |
| H | -1.291182 | 0.218458 | -1.567974 |
| H | -0.077144 | 0.031703 | -2.850758 |
| H | -0.167058 | 1.555124 | -1.917406 |
| H | 0.102855 | 3.315228 | -6.805104 |

**TS_GVL(OTf)**

55

| | | | |
|---|---|---|---|
| C | -4.047318 | 8.194619 | -8.570270 |
| C | -3.562011 | 9.318448 | -7.686584 |
| O | -2.583445 | 10.010836 | -8.283992 |
| C | -2.311114 | 9.475983 | -9.650154 |
| C | -2.954993 | 8.077722 | -9.637963 |
| O | -3.954706 | 9.638923 | -6.565350 |
| C | -2.875415 | 10.442366 | -10.673041 |
| O | -5.930887 | 8.361322 | -5.296699 |
| C | -6.842010 | 9.355795 | -4.778660 |
| C | -5.092438 | 7.176933 | -3.882655 |
| C | -4.156890 | 8.140328 | -3.299745 |
| C | -5.635850 | 6.021213 | -3.966152 |
| C | -6.701514 | 5.434626 | -4.836986 |
| Au | -4.739635 | 4.818781 | -2.494897 |
| C | -3.979187 | 3.530528 | -1.121508 |
| N | -4.380897 | 3.364398 | 0.168824 |
| C | -3.635499 | 2.379938 | 0.790774 |
| C | -2.746940 | 1.917917 | -0.132042 |
| N | -2.971586 | 2.631458 | -1.294779 |
| C | -5.450714 | 4.115815 | 0.820581 |
| C | -2.220804 | 2.435630 | -2.532490 |
| H | -6.355816 | 10.000795 | -4.033815 |
| H | -7.681330 | 8.827212 | -4.316538 |
| H | -5.177054 | 8.828944 | -5.770006 |
| H | -1.984761 | 1.153417 | -0.062817 |
| H | -3.798793 | 2.097731 | 1.822251 |
| H | -3.621104 | 7.655225 | -2.473585 |
| H | -4.677783 | 9.015808 | -2.890168 |
| H | -3.414966 | 8.481404 | -4.033454 |
| H | -6.332114 | 4.535683 | -5.347065 |
| H | -7.037957 | 6.160619 | -5.585558 |
| H | -7.560222 | 5.122422 | -4.228391 |
| H | -2.360749 | 1.411551 | -2.894372 |
| H | -1.156333 | 2.620392 | -2.354112 |
| H | -2.597293 | 3.143198 | -3.276632 |
| H | -5.845580 | 4.839798 | 0.102142 |
| H | -5.054893 | 4.643148 | 1.694665 |
| H | -6.248359 | 3.433451 | 1.132463 |
| H | -7.210381 | 9.974579 | -5.606894 |
| H | -4.212284 | 7.284472 | -7.984780 |
| H | -5.021112 | 8.494843 | -8.984645 |
| H | -2.216211 | 7.323583 | -9.344154 |
| H | -3.345878 | 7.809454 | -10.624442 |
| H | -1.219610 | 9.433489 | -9.714458 |
| H | -2.469436 | 11.450060 | -10.524147 |
| H | -2.591631 | 10.103419 | -11.677702 |
| H | -3.971402 | 10.489014 | -10.621103 |
| O | -10.289022 | 6.600978 | -1.716083 |

| | | | |
|---|---|---|---|
| S | -10.817159 | 7.347689 | -2.868855 |
| C | -12.540410 | 7.859778 | -2.298012 |
| O | -11.091871 | 6.531371 | -4.063196 |
| O | -10.153106 | 8.633707 | -3.134722 |
| F | -13.175944 | 8.574661 | -3.257701 |
| F | -13.297815 | 6.772720 | -2.014443 |
| F | -12.471849 | 8.625163 | -1.181958 |

**PC_GVL(OTf)**

55

| | | | |
|---|---|---|---|
| C | -3.980461 | 8.088239 | -8.152166 |
| C | -3.600104 | 9.435233 | -7.599007 |
| O | -2.782832 | 10.090181 | -8.404164 |
| C | -2.532383 | 9.298925 | -9.656850 |
| C | -2.962299 | 7.871505 | -9.277895 |
| O | -3.963531 | 9.960796 | -6.531889 |
| C | -3.310019 | 9.938162 | -10.788365 |
| O | -5.645710 | 8.741207 | -5.190770 |
| C | -6.694872 | 9.655683 | -4.712820 |
| C | -5.085019 | 7.789168 | -4.160945 |
| C | -4.121326 | 8.494565 | -3.266322 |
| C | -5.519715 | 6.528441 | -4.200244 |
| C | -6.524489 | 6.049477 | -5.221361 |
| Au | -4.915513 | 5.165045 | -2.776530 |
| C | -4.408720 | 3.779229 | -1.352185 |
| N | -4.980756 | 3.613695 | -0.125280 |
| C | -4.375916 | 2.582156 | 0.570491 |
| C | -3.401532 | 2.082819 | -0.239105 |
| N | -3.436650 | 2.824781 | -1.406727 |
| C | -6.075142 | 4.425824 | 0.401278 |
| C | -2.555726 | 2.596108 | -2.548801 |
| H | -6.303498 | 10.288644 | -3.910625 |
| H | -7.524886 | 9.037410 | -4.362158 |
| H | -4.879192 | 9.268124 | -5.751787 |
| H | -2.700825 | 1.272023 | -0.089716 |
| H | -4.688821 | 2.293829 | 1.565401 |
| H | -3.722105 | 7.776012 | -2.542089 |
| H | -4.595113 | 9.314561 | -2.705605 |
| H | -3.277731 | 8.923681 | -3.828214 |
| H | -6.147852 | 5.154759 | -5.737289 |
| H | -6.784526 | 6.801327 | -5.978658 |
| H | -7.451562 | 5.742485 | -4.715400 |
| H | -2.708348 | 1.585086 | -2.942222 |
| H | -1.510320 | 2.717331 | -2.245290 |
| H | -2.803126 | 3.331680 | -3.319808 |
| H | -6.485426 | 5.022892 | -0.419004 |
| H | -5.708104 | 5.088633 | 1.193270 |

| | | | |
|---|---|---|---|
| H | -6.854744 | 3.771661 | 0.805300 |
| H | -6.990164 | 10.259595 | -5.574333 |
| H | -3.962870 | 7.324432 | -7.367352 |
| H | -5.015988 | 8.156628 | -8.517255 |
| H | -2.103369 | 7.302264 | -8.906736 |
| H | -3.383821 | 7.340073 | -10.136360 |
| H | -1.454417 | 9.388105 | -9.816657 |
| H | -3.045645 | 10.996450 | -10.896958 |
| H | -3.056747 | 9.423196 | -11.723767 |
| H | -4.393502 | 9.854531 | -10.630983 |
| O | -8.932137 | 5.947032 | -1.758689 |
| S | -9.821158 | 6.576596 | -2.745112 |
| C | -11.418772 | 6.827643 | -1.778116 |
| O | -10.237930 | 5.701679 | -3.856218 |
| O | -9.456114 | 7.946588 | -3.142213 |
| F | -12.364518 | 7.424481 | -2.542322 |
| F | -11.915396 | 5.642638 | -1.346955 |
| F | -11.202641 | 7.610050 | -0.692495 |

**TS_GVL(OTf)'**

55

| | | | |
|---|---|---|---|
| O | -10.714812 | 10.894280 | -1.449954 |
| C | -9.383459 | 10.759899 | -1.472733 |
| C | -8.967389 | 9.399706 | -0.965499 |
| C | -10.270334 | 8.593601 | -0.985795 |
| C | -11.361908 | 9.673658 | -0.882639 |
| O | -8.671122 | 11.683635 | -1.866142 |
| C | -11.838917 | 9.986854 | 0.521913 |
| O | -6.010014 | 11.500614 | -1.906235 |
| C | -5.458680 | 12.694912 | -1.310075 |
| C | -5.448200 | 11.191860 | -3.825470 |
| C | -6.275468 | 12.210091 | -4.474984 |
| C | -4.598033 | 10.234765 | -3.838904 |
| C | -3.984925 | 9.378770 | -2.775436 |
| Au | -4.054450 | 9.913245 | -5.842733 |
| C | -3.430915 | 9.465672 | -7.723470 |
| N | -3.981397 | 8.565497 | -8.584154 |
| C | -3.270077 | 8.522196 | -9.768872 |
| C | -2.248758 | 9.414575 | -9.646592 |
| N | -2.361785 | 9.981249 | -8.390415 |
| C | -5.160653 | 7.749155 | -8.308166 |
| C | -1.452202 | 10.997384 | -7.866931 |
| H | -5.716378 | 13.592997 | -1.887906 |
| H | -4.371911 | 12.575083 | -1.282939 |
| H | -7.014183 | 11.568265 | -1.902594 |
| H | -3.548553 | 7.869349 | -10.585227 |
| H | -1.462733 | 9.692606 | -10.335858 |

| | | | |
|---|---|---|---|
| H | -6.060235 | 12.204966 | -5.551380 |
| H | -6.054524 | 13.216183 | -4.095244 |
| H | -7.346438 | 12.009393 | -4.340407 |
| H | -4.178909 | 8.317542 | -2.978610 |
| H | -4.385769 | 9.633627 | -1.787936 |
| H | -2.894052 | 9.502950 | -2.765350 |
| H | -4.894625 | 6.687401 | -8.343993 |
| H | -5.938892 | 7.958914 | -9.049383 |
| H | -5.525248 | 8.004531 | -7.309010 |
| H | -1.777151 | 11.259712 | -6.856184 |
| H | -1.480912 | 11.886467 | -8.505612 |
| H | -0.431855 | 10.601210 | -7.834139 |
| H | -5.840822 | 12.798731 | -0.286640 |
| H | -8.164253 | 8.985344 | -1.583838 |
| H | -8.559790 | 9.533080 | 0.047507 |
| H | -10.363164 | 8.048062 | -1.932490 |
| H | -10.342012 | 7.875040 | -0.163168 |
| H | -12.208460 | 9.479353 | -1.548227 |
| H | -12.506175 | 10.856991 | 0.523154 |
| H | -12.398237 | 9.125222 | 0.908484 |
| H | -10.996481 | 10.183270 | 1.198521 |
| O | -10.452016 | 6.980563 | -4.286568 |
| S | -9.591957 | 5.830695 | -4.609044 |
| O | -9.374709 | 4.887892 | -3.497465 |
| O | -8.392224 | 6.147104 | -5.397678 |
| C | -10.650223 | 4.832664 | -5.811142 |
| F | -11.817294 | 4.456066 | -5.233745 |
| F | -10.946688 | 5.562400 | -6.914609 |
| F | -10.003274 | 3.711761 | -6.214489 |

**PC_GVL(OTf)'**

55

| | | | |
|---|---|---|---|
| N | -2.310776 | 9.860173 | -8.287703 |
| C | -3.429689 | 9.400715 | -7.658476 |
| N | -3.996552 | 8.542462 | -8.553577 |
| C | -3.247890 | 8.469046 | -9.714714 |
| C | -2.183520 | 9.301121 | -9.546894 |
| Au | -4.114165 | 9.891698 | -5.788451 |
| C | -4.778148 | 10.340830 | -3.887909 |
| C | -4.284387 | 9.471474 | -2.755072 |
| C | -5.231887 | 7.797505 | -8.328445 |
| C | -1.365190 | 10.816940 | -7.719194 |
| C | -5.610274 | 11.366111 | -3.694614 |
| C | -6.227404 | 12.350058 | -4.632090 |
| O | -6.065324 | 11.626689 | -2.278359 |
| C | -5.399042 | 12.739465 | -1.586111 |
| O | -8.511863 | 11.822496 | -2.019956 |

| | | | |
|---|---|---|---|
| C | -9.190007 | 10.818055 | -1.735918 |
| O | -10.487623 | 10.946388 | -1.536028 |
| C | -11.097826 | 9.631910 | -1.143384 |
| C | -10.036839 | 8.595534 | -1.553741 |
| C | -8.728476 | 9.396391 | -1.564027 |
| C | -11.427946 | 9.684037 | 0.333406 |
| O | -10.771302 | 6.747669 | -4.748523 |
| S | -9.727704 | 5.757680 | -5.065966 |
| C | -10.542360 | 4.687460 | -6.389282 |
| F | -9.704209 | 3.703502 | -6.798153 |
| O | -9.443301 | 4.792729 | -3.989207 |
| O | -8.541942 | 6.296864 | -5.746289 |
| F | -11.671673 | 4.105343 | -5.917245 |
| F | -10.876372 | 5.428666 | -7.473510 |
| H | -5.537732 | 13.668462 | -2.146416 |
| H | -4.342114 | 12.478638 | -1.508274 |
| H | -7.150540 | 11.699438 | -2.192010 |
| H | -3.532464 | 7.840738 | -10.548335 |
| H | -1.358643 | 9.539829 | -10.205138 |
| H | -5.886715 | 12.129334 | -5.649707 |
| H | -5.944489 | 13.387039 | -4.395179 |
| H | -7.326381 | 12.296783 | -4.617917 |
| H | -4.522570 | 8.416940 | -2.956243 |
| H | -4.701184 | 9.735627 | -1.773749 |
| H | -3.187652 | 9.523708 | -2.688202 |
| H | -5.038764 | 6.722024 | -8.405765 |
| H | -5.985082 | 8.089264 | -9.068530 |
| H | -5.592119 | 8.035405 | -7.323169 |
| H | -1.707825 | 11.076255 | -6.713282 |
| H | -1.327501 | 11.719228 | -8.339249 |
| H | -0.367333 | 10.368393 | -7.664565 |
| H | -5.858669 | 12.807604 | -0.597452 |
| H | -8.028094 | 9.116169 | -2.358665 |
| H | -8.178976 | 9.337372 | -0.612936 |
| H | -10.252440 | 8.199386 | -2.552643 |
| H | -10.011376 | 7.756862 | -0.851042 |
| H | -12.005924 | 9.570604 | -1.749504 |
| H | -12.078931 | 10.536583 | 0.559293 |
| H | -11.959997 | 8.764245 | 0.607434 |
| H | -10.519843 | 9.754306 | 0.946737 |

**RC_OTf(NM)**

47

| | | | |
|---|---|---|---|
| C | -2.297647 | 2.439332 | -1.912337 |
| N | -3.034796 | 3.472015 | -2.403846 |
| C | -4.346732 | 3.085666 | -2.583315 |
| C | -4.432841 | 1.781906 | -2.193276 |

| | | | |
|---|---|---|---|
| N | -3.170904 | 1.403042 | -1.785358 |
| C | -2.522259 | 4.801668 | -2.733345 |
| C | -2.839349 | 0.070211 | -1.285496 |
| Au | -0.326666 | 2.442742 | -1.467954 |
| C | 1.616875 | 2.682401 | -0.428590 |
| C | 1.664624 | 3.227077 | 0.929371 |
| C | 1.877223 | 2.218599 | -1.550415 |
| C | 2.535513 | 1.689461 | -2.747094 |
| O | 0.399287 | 6.531744 | -1.677797 |
| S | 0.658655 | 7.193985 | -0.394898 |
| O | 0.055623 | 6.564219 | 0.787235 |
| O | 2.062672 | 7.628168 | -0.212279 |
| C | -0.270127 | 8.827676 | -0.546594 |
| F | 0.189953 | 9.543819 | -1.601578 |
| F | -0.118088 | 9.578305 | 0.569056 |
| F | -1.592729 | 8.610156 | -0.732242 |
| O | 3.434111 | 7.940840 | 2.203625 |
| C | 3.974265 | 9.270250 | 2.202893 |
| H | 4.639313 | 9.439779 | 1.341473 |
| H | 4.558424 | 9.386863 | 3.123169 |
| H | 2.907337 | 7.830170 | 1.376192 |
| H | -5.276040 | 1.104504 | -2.167966 |
| H | -5.099712 | 3.762241 | -2.964829 |
| H | 1.231226 | 4.235429 | 0.965277 |
| H | 2.713730 | 3.280520 | 1.252222 |
| H | 1.116432 | 2.589542 | 1.633680 |
| H | 2.202887 | 0.667319 | -2.965684 |
| H | 3.620593 | 1.675137 | -2.576693 |
| H | 2.330007 | 2.314533 | -3.624536 |
| H | -3.036282 | -0.674923 | -2.063112 |
| H | -3.442766 | -0.151892 | -0.399512 |
| H | -1.778674 | 0.054564 | -1.020726 |
| H | -1.543252 | 4.936188 | -2.263981 |
| H | -3.216691 | 5.555867 | -2.351513 |
| H | -2.429660 | 4.906432 | -3.819994 |
| H | 3.180889 | 10.033929 | 2.194043 |
| O | 7.706262 | 13.540217 | 1.906852 |
| N | 8.757711 | 12.984024 | 2.243074 |
| O | 8.845271 | 12.167681 | 3.165061 |
| C | 9.997898 | 13.346931 | 1.492315 |
| H | 10.791660 | 12.660160 | 1.783818 |
| H | 9.763618 | 13.290368 | 0.427028 |
| H | 10.235989 | 14.378764 | 1.768644 |

**TS_OTf(NM)**

47

| | | | |
|---|---|---|---|
| C | -3.210026 | 0.997840 | -2.317748 |

| | | | |
|---|---|---|---|
| C | -3.218500 | 2.311498 | -2.675839 |
| N | -4.544840 | 2.692623 | -2.762948 |
| C | -5.367095 | 1.647476 | -2.470499 |
| N | -4.531326 | 0.608359 | -2.196950 |
| C | -4.987292 | 4.033601 | -3.135492 |
| Au | -7.397395 | 1.643429 | -2.425279 |
| C | -9.486713 | 1.562441 | -2.222300 |
| C | -10.068104 | 0.882842 | -1.021730 |
| C | -4.955243 | -0.735873 | -1.813131 |
| C | -9.990376 | 2.155417 | -3.239487 |
| C | -9.891498 | 2.875138 | -4.509274 |
| O | -12.000877 | 2.123622 | -3.031850 |
| C | -12.762118 | 1.549737 | -4.115771 |
| O | -12.814003 | 4.601380 | -2.443766 |
| S | -12.840936 | 5.854910 | -3.239982 |
| C | -14.604294 | 5.882472 | -3.909223 |
| F | -14.845543 | 4.791871 | -4.671418 |
| O | -12.008238 | 5.826333 | -4.448179 |
| O | -12.756399 | 7.071568 | -2.426361 |
| F | -14.804314 | 6.984020 | -4.667473 |
| F | -15.499214 | 5.896342 | -2.894986 |
| H | -13.823135 | 1.526362 | -3.836580 |
| H | -12.402562 | 0.526833 | -4.260556 |
| H | -12.280248 | 3.077952 | -2.900195 |
| H | -2.388965 | 0.315882 | -2.141409 |
| H | -2.406421 | 2.998062 | -2.874613 |
| H | -10.380280 | 3.857449 | -4.457082 |
| H | -10.333970 | 2.303462 | -5.335742 |
| H | -8.830138 | 3.028037 | -4.743815 |
| H | -9.733272 | -0.161598 | -0.973604 |
| H | -11.163008 | 0.907519 | -1.048917 |
| H | -9.719756 | 1.368840 | -0.100951 |
| H | -4.627688 | -0.953510 | -0.790877 |
| H | -4.524882 | -1.469875 | -2.502182 |
| H | -6.046670 | -0.779427 | -1.866280 |
| H | -6.077730 | 4.066685 | -3.057868 |
| H | -4.685549 | 4.255377 | -4.164710 |
| H | -4.547099 | 4.770042 | -2.455250 |
| H | -12.640526 | 2.119490 | -5.046314 |
| O | -8.682982 | 8.337662 | 0.455067 |
| N | -8.175047 | 8.912131 | -0.513892 |
| O | -7.182529 | 8.498881 | -1.122365 |
| C | -8.780414 | 10.202360 | -0.966234 |
| H | -9.793879 | 10.264741 | -0.570194 |
| H | -8.148999 | 10.996086 | -0.554445 |
| H | -8.744509 | 10.224780 | -2.056916 |

**PC_OTf(NM)**

47

| | | | |
|---|---|---|---|
| N | -4.487657 | 0.577148 | -2.073976 |
| C | -3.158530 | 0.942819 | -2.189307 |
| C | -3.143891 | 2.231795 | -2.627551 |
| N | -4.464584 | 2.618822 | -2.767134 |
| C | -5.311003 | 1.604584 | -2.428146 |
| C | -4.884320 | 3.941236 | -3.222474 |
| Au | -7.361359 | 1.628793 | -2.446635 |
| C | -9.423711 | 1.655424 | -2.409353 |
| C | -10.098003 | 2.209806 | -3.419542 |
| C | -9.652435 | 2.847200 | -4.692511 |
| C | -4.936815 | -0.738196 | -1.625767 |
| C | -10.107537 | 1.061380 | -1.199610 |
| O | -11.600700 | 2.261657 | -3.279602 |
| C | -12.409758 | 1.658131 | -4.345158 |
| O | -12.484864 | 4.425828 | -2.464908 |
| S | -12.547449 | 5.737070 | -3.197521 |
| O | -12.295262 | 6.878090 | -2.322043 |
| C | -14.381359 | 5.864316 | -3.622015 |
| F | -15.129965 | 5.865209 | -2.499639 |
| O | -11.870936 | 5.718572 | -4.494276 |
| F | -14.761615 | 4.823349 | -4.392675 |
| F | -14.614016 | 7.009300 | -4.296970 |
| O | -8.198310 | 8.371420 | 0.443357 |
| N | -7.770625 | 8.924145 | -0.575865 |
| C | -8.414425 | 10.203310 | -1.004819 |
| O | -6.827679 | 8.499288 | -1.250663 |
| H | -13.443015 | 1.686651 | -3.992476 |
| H | -12.068917 | 0.627188 | -4.458448 |
| H | -11.957894 | 3.238336 | -3.008356 |
| H | -2.349055 | 0.265089 | -1.952297 |
| H | -2.319448 | 2.897008 | -2.847601 |
| H | -10.027055 | 3.877576 | -4.782017 |
| H | -9.989512 | 2.291746 | -5.580519 |
| H | -8.557629 | 2.867725 | -4.707797 |
| H | -9.771394 | 0.025789 | -1.044226 |
| H | -11.203735 | 1.063647 | -1.261746 |
| H | -9.814982 | 1.611930 | -0.292889 |
| H | -4.585828 | -0.925481 | -0.605115 |
| H | -4.549202 | -1.513515 | -2.295425 |
| H | -6.030314 | -0.749216 | -1.646414 |
| H | -5.977310 | 3.977535 | -3.196381 |
| H | -4.534457 | 4.115013 | -4.246007 |
| H | -4.474151 | 4.710765 | -2.559517 |
| H | -12.295135 | 2.217944 | -5.277465 |
| H | -9.420163 | 10.238405 | -0.585942 |
| H | -7.794603 | 11.006904 | -0.594039 |
| H | -8.401565 | 10.238948 | -2.095188 |

**RC_NM(OTf)**

47

| | | | |
|---|---|---|---|
| N | -1.807642 | 1.401145 | -3.396858 |
| C | -1.109775 | 1.933555 | -4.436641 |
| N | -1.848831 | 2.995397 | -4.858472 |
| C | -2.992211 | 3.120648 | -4.097463 |
| C | -2.965907 | 2.116380 | -3.175041 |
| Au | 0.638085 | 1.276473 | -5.207382 |
| C | 2.176558 | 0.167903 | -6.355671 |
| C | 1.798464 | -0.909672 | -7.273084 |
| C | -1.521204 | 3.854648 | -5.996854 |
| C | -1.403979 | 0.236185 | -2.611382 |
| C | 2.790867 | 1.003662 | -5.673246 |
| C | 3.802719 | 1.847779 | -5.035940 |
| O | 3.969783 | 5.207486 | -6.162368 |
| S | 2.785047 | 6.000155 | -6.530320 |
| C | 2.207811 | 6.700513 | -4.877050 |
| F | 1.897553 | 5.710303 | -4.008134 |
| O | 1.627542 | 5.217688 | -6.990213 |
| O | 3.068671 | 7.210947 | -7.321257 |
| F | 1.106659 | 7.473917 | -5.038986 |
| F | 3.175207 | 7.463614 | -4.314469 |
| C | 5.346260 | 8.575003 | -9.443593 |
| N | 6.612615 | 9.197419 | -8.961037 |
| O | 6.515066 | 10.052147 | -8.064071 |
| O | 7.679935 | 8.847495 | -9.462423 |
| O | 8.975729 | 11.460639 | -7.399291 |
| C | 8.555724 | 12.734373 | -6.881664 |
| H | 8.009696 | 13.320570 | -7.636792 |
| H | 9.460085 | 13.285073 | -6.599554 |
| H | -3.661063 | 1.859031 | -2.387368 |
| H | -3.715820 | 3.905865 | -4.270368 |
| H | 3.684438 | 2.899760 | -5.329298 |
| H | 4.796787 | 1.505740 | -5.356315 |
| H | 3.748824 | 1.778680 | -3.942629 |
| H | 1.301455 | -1.729339 | -6.740188 |
| H | 2.707043 | -1.303174 | -7.749021 |
| H | 1.123288 | -0.547512 | -8.057632 |
| H | -2.145521 | -0.561047 | -2.726099 |
| H | -1.320960 | 0.514218 | -1.555938 |
| H | -0.433520 | -0.108679 | -2.978113 |
| H | -0.434442 | 3.941173 | -6.088611 |
| H | -1.951833 | 4.844199 | -5.822120 |
| H | -1.940650 | 3.433742 | -6.917205 |
| H | 7.920851 | 12.621640 | -5.989407 |
| H | 8.169807 | 10.953930 | -7.641397 |

| | | | |
|---|---|---|---|
| H | 4.727814 | 9.386385 | -9.836289 |
| H | 4.847914 | 8.118441 | -8.580903 |
| H | 5.596932 | 7.845096 | -10.211401 |

**TS_NM(OTf)**

47

| | | | |
|---|---|---|---|
| C | -3.338076 | 8.218165 | -9.907958 |
| N | -4.079024 | 8.169159 | -8.741600 |
| C | -3.670797 | 9.132077 | -7.869844 |
| N | -2.660527 | 9.781512 | -8.511629 |
| C | -2.443897 | 9.234895 | -9.762991 |
| C | -5.154173 | 7.211163 | -8.495752 |
| Au | -4.390524 | 9.502898 | -6.005925 |
| C | -5.027209 | 9.772844 | -4.025722 |
| C | -5.892427 | 10.721544 | -4.000726 |
| C | -6.703895 | 11.735979 | -4.679973 |
| C | -1.899109 | 10.902343 | -7.965668 |
| C | -4.439419 | 8.905974 | -2.954707 |
| O | -6.477362 | 10.999836 | -2.139050 |
| C | -5.898858 | 12.172189 | -1.513722 |
| O | -9.214112 | 11.382382 | -2.139090 |
| N | -9.913630 | 10.476510 | -1.639588 |
| C | -11.385173 | 10.710373 | -1.613759 |
| O | -9.458483 | 9.432745 | -1.188178 |
| O | -1.385114 | 14.026173 | -0.656304 |
| S | -0.157060 | 13.240148 | -0.856025 |
| C | 1.148653 | 14.232708 | 0.076453 |
| F | 2.360708 | 13.634041 | -0.007726 |
| O | -0.135178 | 11.935835 | -0.174351 |
| O | 0.351184 | 13.225696 | -2.238009 |
| F | 1.261329 | 15.482658 | -0.433161 |
| F | 0.824678 | 14.341593 | 1.387263 |
| H | -6.118609 | 13.082662 | -2.085713 |
| H | -4.818674 | 12.010580 | -1.470793 |
| H | -7.470273 | 11.097111 | -2.146933 |
| H | -3.509352 | 7.535558 | -10.729477 |
| H | -1.682125 | 9.610675 | -10.432959 |
| H | -6.446724 | 11.731160 | -5.746860 |
| H | -6.506628 | 12.744568 | -4.293563 |
| H | -7.777985 | 11.525768 | -4.590407 |
| H | -4.619541 | 7.846539 | -3.179645 |
| H | -4.867058 | 9.138542 | -1.972909 |
| H | -3.349952 | 9.035838 | -2.913551 |
| H | -4.759840 | 6.190548 | -8.540702 |
| H | -5.940890 | 7.334770 | -9.247368 |
| H | -5.563239 | 7.403897 | -7.499953 |
| H | -2.298369 | 11.135739 | -6.974492 |

H -2.002796 11.775498 -8.618442
H -0.842039 10.628718 -7.881493
H -6.298083 12.266941 -0.497324
H -11.853849 9.871572 -1.101656
H -11.550442 11.660391 -1.099585
H -11.710092 10.790739 -2.655051

**PC_NM(OTf)**

47

N -4.820191 7.921686 -8.492066
C -4.154940 9.024626 -8.044823
N -3.317345 9.357126 -9.067668
C -3.456967 8.480594 -10.128742
C -4.406185 7.574406 -9.765353
Au -4.366740 9.974202 -6.240754
C -4.529629 10.908517 -4.406883
C -3.521611 10.541004 -3.344333
C -2.389083 10.484300 -9.055372
C -5.836895 7.194755 -7.737103
C -5.495876 11.802723 -4.210364
C -6.594678 12.335453 -5.065091
O -5.549535 12.458403 -2.824878
C -4.981743 13.819290 -2.727900
O -7.952563 12.469122 -1.848358
N -8.179272 11.606581 -0.959474
O -7.347551 10.807308 -0.567568
O -1.546310 14.654266 -2.652940
S -0.238753 14.057488 -2.970103
O 0.218524 13.025931 -2.023812
O -0.033211 13.729974 -4.389929
C 0.968763 15.476608 -2.673690
F 0.679369 16.530607 -3.474544
F 0.912203 15.899458 -1.387973
F 2.240232 15.089103 -2.932710
H -5.445664 14.468093 -3.475321
H -3.905899 13.723897 -2.888803
H -6.508456 12.438590 -2.437097
H -4.817237 6.725733 -10.295805
H -2.877814 8.576579 -11.037420
H -6.537414 11.854381 -6.047633
H -6.520088 13.422941 -5.214160
H -7.587183 12.125031 -4.638080
H -3.511465 9.452447 -3.192589
H -3.700353 11.021357 -2.373301
H -2.509074 10.808379 -3.680254
H -5.519683 6.156983 -7.586762
H -6.788696 7.212181 -8.279134

| | | | |
|---|---|---|---|
| H | -5.956669 | 7.686246 | -6.767043 |
| H | -2.507024 | 11.010437 | -8.103680 |
| H | -2.616880 | 11.164859 | -9.882769 |
| H | -1.359543 | 10.122416 | -9.151345 |
| H | -5.197394 | 14.167858 | -1.715214 |
| C | -9.554093 | 11.602698 | -0.393076 |
| H | -9.608630 | 10.809289 | 0.350374 |
| H | -9.722965 | 12.592870 | 0.039062 |
| H | -10.241128 | 11.440576 | -1.228352 |

**TS_NM(OTf)'**

47

| | | | |
|---|---|---|---|
| C | -3.987682 | 8.121897 | -8.848437 |
| N | -3.736540 | 9.131098 | -7.937149 |
| C | -2.655966 | 9.866532 | -8.317628 |
| N | -2.236659 | 9.298837 | -9.482137 |
| C | -3.043251 | 8.228732 | -9.823461 |
| C | -4.523555 | 9.354538 | -6.726923 |
| Au | -1.833584 | 11.444869 | -7.337756 |
| C | -0.990082 | 12.979343 | -6.181578 |
| C | -0.599282 | 13.917634 | -6.966243 |
| C | -0.459870 | 14.497273 | -8.304094 |
| C | -1.101192 | 9.753549 | -10.280334 |
| C | -0.931809 | 12.799234 | -4.695070 |
| O | 0.294159 | 15.308458 | -5.873690 |
| C | -0.122858 | 16.684612 | -6.045883 |
| O | 5.134755 | 14.989242 | -10.910427 |
| S | 5.004798 | 13.559687 | -10.583929 |
| C | 6.296033 | 12.743475 | -11.691325 |
| F | 6.300200 | 11.400044 | -11.515599 |
| O | 5.449214 | 13.188564 | -9.229414 |
| O | 3.744741 | 12.935643 | -11.015909 |
| F | 6.041649 | 12.994618 | -12.997899 |
| F | 7.537134 | 13.207155 | -11.409440 |
| H | -1.193313 | 16.726032 | -5.827831 |
| H | 0.065747 | 17.040161 | -7.066354 |
| H | 1.259124 | 15.222533 | -6.114724 |
| H | -4.805751 | 7.424601 | -8.726434 |
| H | -2.878019 | 7.643967 | -10.718520 |
| H | -0.927732 | 13.817523 | -9.027408 |
| H | 0.593161 | 14.628899 | -8.586547 |
| H | -0.970617 | 15.465411 | -8.385536 |
| H | -1.938714 | 12.630772 | -4.291541 |
| H | -0.490906 | 13.674136 | -4.205154 |
| H | -0.338663 | 11.910088 | -4.443167 |
| H | -4.417064 | 8.500980 | -6.048788 |
| H | -5.577894 | 9.486360 | -6.990811 |

| | | | |
|---|---|---|---|
| H | -4.152000 | 10.259894 | -6.238806 |
| H | -0.604546 | 10.562032 | -9.736433 |
| H | -1.448963 | 10.120314 | -11.252016 |
| H | -0.398545 | 8.927108 | -10.428436 |
| H | 0.423815 | 17.309861 | -5.330042 |
| O | 2.894734 | 14.811697 | -6.591272 |
| N | 3.801664 | 15.542690 | -6.146123 |
| O | 3.600389 | 16.526658 | -5.440929 |
| C | 5.203383 | 15.163705 | -6.479608 |
| H | 5.197943 | 14.621366 | -7.428634 |
| H | 5.797892 | 16.077749 | -6.501349 |
| H | 5.538691 | 14.511185 | -5.665957 |

**PC_NM(OTf)'**

47

| | | | |
|---|---|---|---|
| C | -3.416655 | 8.256501 | -9.890371 |
| C | -4.268236 | 8.121531 | -8.836308 |
| N | -3.904201 | 9.077740 | -7.905519 |
| C | -2.843679 | 9.811537 | -8.347881 |
| N | -2.554899 | 9.291225 | -9.574788 |
| C | -4.572725 | 9.262704 | -6.619998 |
| Au | -1.890348 | 11.344995 | -7.378932 |
| C | -0.926609 | 12.850385 | -6.345915 |
| C | -0.869237 | 12.732476 | -4.841143 |
| C | -1.484027 | 9.757374 | -10.451393 |
| C | -0.377401 | 13.862484 | -7.016437 |
| C | -0.296286 | 14.207511 | -8.464087 |
| O | 0.362594 | 14.909044 | -6.179079 |
| C | -0.231430 | 16.259054 | -6.115648 |
| O | 2.823456 | 14.817551 | -6.929818 |
| N | 3.650175 | 15.515778 | -6.293026 |
| C | 5.079189 | 15.389649 | -6.683229 |
| O | 3.337426 | 16.269215 | -5.384806 |
| O | 5.569129 | 13.144839 | -9.301951 |
| S | 5.044739 | 13.342604 | -10.664177 |
| O | 3.792515 | 12.627039 | -10.956996 |
| O | 5.095717 | 14.731116 | -11.151538 |
| C | 6.311931 | 12.458446 | -11.747490 |
| F | 7.545381 | 12.993855 | -11.583827 |
| F | 6.379068 | 11.143131 | -11.431423 |
| F | 5.981330 | 12.558253 | -13.057482 |
| H | -1.233064 | 16.133360 | -5.702285 |
| H | -0.261003 | 16.704132 | -7.113509 |
| H | 1.363413 | 14.949254 | -6.459631 |
| H | -5.088661 | 7.435868 | -8.670850 |
| H | -3.350599 | 7.713014 | -10.823657 |
| H | -0.801684 | 13.423804 | -9.038120 |

| | | | |
|---|---|---|---|
| H | 0.744993 | 14.274850 | -8.813584 |
| H | -0.787534 | 15.163682 | -8.695423 |
| H | -1.886970 | 12.672712 | -4.429315 |
| H | -0.345154 | 13.561085 | -4.348070 |
| H | -0.373674 | 11.793133 | -4.556187 |
| H | -4.479778 | 8.354012 | -6.015327 |
| H | -5.632070 | 9.490947 | -6.779865 |
| H | -4.092108 | 10.098235 | -6.103284 |
| H | -0.936259 | 10.545487 | -9.926858 |
| H | -1.905973 | 10.155896 | -11.380545 |
| H | -0.804798 | 8.929722 | -10.682048 |
| H | 0.404368 | 16.836851 | -5.441595 |
| H | 5.145528 | 14.759835 | -7.571416 |
| H | 5.451670 | 16.403696 | -6.845891 |
| H | 5.591308 | 14.942585 | -5.825789 |

**RC COSMO NM**

40

| | | | |
|---|---|---|---|
| N | -2.861211 | 4.098790 | -2.531252 |
| C | -4.151183 | 3.692516 | -2.677958 |
| N | -4.155633 | 2.377403 | -2.327847 |
| C | -2.888982 | 1.969962 | -1.965382 |
| C | -2.072562 | 3.053862 | -2.096532 |
| Au | -5.731438 | 4.802744 | -3.274024 |
| C | -7.592913 | 6.005481 | -3.304766 |
| C | -8.314781 | 6.304829 | -2.065350 |
| C | -5.328391 | 1.505470 | -2.317599 |
| C | -2.354638 | 5.441561 | -2.810022 |
| C | -7.216417 | 5.918261 | -4.484744 |
| C | -7.049355 | 6.040887 | -5.934209 |
| O | -6.661949 | 10.840796 | -7.073617 |
| C | -6.491455 | 12.260564 | -7.194457 |
| O | -5.117014 | 10.084409 | -4.872032 |
| S | -4.027767 | 9.085499 | -4.790196 |
| O | -3.771823 | 8.590923 | -3.432203 |
| C | -2.492889 | 10.109016 | -5.180260 |
| F | -2.350625 | 11.121629 | -4.291925 |
| O | -4.039996 | 8.072222 | -5.852496 |
| H | -6.789229 | 12.789177 | -6.274941 |
| H | -7.134072 | 12.601049 | -8.014105 |
| H | -6.092274 | 10.533712 | -6.328592 |
| H | -2.677390 | 0.957303 | -1.649564 |
| H | -1.011135 | 3.166936 | -1.920578 |
| H | -6.143988 | 6.615502 | -6.170090 |
| H | -7.920931 | 6.566991 | -6.347150 |
| H | -6.978857 | 5.057799 | -6.414758 |
| H | -8.658226 | 5.386987 | -1.572554 |

| | | | |
|---|---|---|---|
| H | -9.192496 | 6.919258 | -2.307247 |
| H | -7.683125 | 6.859566 | -1.360513 |
| H | -5.546491 | 1.189103 | -1.292453 |
| H | -5.138291 | 0.627674 | -2.943230 |
| H | -6.178069 | 2.064333 | -2.718753 |
| H | -3.191475 | 6.091879 | -3.080458 |
| H | -1.640815 | 5.399069 | -3.639670 |
| H | -1.857487 | 5.835220 | -1.917478 |
| H | -5.450197 | 12.528616 | -7.433608 |
| F | -2.572849 | 10.647508 | -6.419914 |
| F | -1.378614 | 9.342646 | -5.125585 |

**TS COSMO NM**

40

| | | | |
|---|---|---|---|
| C | 6.116478 | 1.155519 | -0.156651 |
| C | 5.442752 | 2.327137 | -0.322523 |
| N | 4.094731 | 2.022887 | -0.272039 |
| C | 3.908822 | 0.687441 | -0.082647 |
| N | 5.163591 | 0.164006 | -0.012232 |
| C | 3.027877 | 3.008928 | -0.424531 |
| AU | 2.146150 | -0.307750 | 0.082590 |
| C | 0.383792 | -1.407226 | 0.396833 |
| C | 0.322025 | -2.355441 | 1.554172 |
| C | 5.477011 | -1.247468 | 0.196415 |
| C | -0.443244 | -1.070645 | -0.522075 |
| C | -0.826015 | -0.310076 | -1.711632 |
| O | -2.160133 | -2.079146 | -0.195455 |
| C | -2.788856 | -2.729729 | -1.320644 |
| O | -3.849166 | -0.376035 | 0.982410 |
| S | -4.456911 | 0.868065 | 0.445797 |
| C | -6.166028 | 0.294011 | -0.106717 |
| F | -6.062564 | -0.669945 | -1.048669 |
| O | -3.836750 | 1.367308 | -0.787123 |
| O | -4.742899 | 1.875122 | 1.474547 |
| F | -6.863851 | 1.327071 | -0.628950 |
| F | -6.862833 | -0.206515 | 0.938120 |
| H | -3.658940 | -3.296112 | -0.964945 |
| H | -2.057587 | -3.420126 | -1.750776 |
| H | -2.792225 | -1.397233 | 0.181931 |
| H | 7.177230 | 0.944849 | -0.128726 |
| H | 5.801237 | 3.337140 | -0.470019 |
| H | -1.707740 | 0.316979 | -1.520993 |
| H | -1.033576 | -0.967889 | -2.565774 |
| H | 0.009979 | 0.343268 | -1.992746 |
| H | 1.139244 | -3.085929 | 1.495712 |
| H | -0.634903 | -2.888120 | 1.575878 |
| H | 0.451643 | -1.811585 | 2.499275 |

| | | | |
|---|---|---|---|
| H | 6.005368 | -1.376254 | 1.147090 |
| H | 6.101731 | -1.613268 | -0.625106 |
| H | 4.537679 | -1.807024 | 0.218897 |
| H | 2.070782 | 2.507584 | -0.256052 |
| H | 3.050558 | 3.431909 | -1.434771 |
| H | 3.155956 | 3.808686 | 0.312122 |
| H | -3.108431 | -2.007262 | -2.082731 |

**PC COSMO NM**

40

| | | | |
|---|---|---|---|
| N | -4.091913 | 2.081881 | -2.411665 |
| C | -5.276527 | 2.658493 | -2.763847 |
| N | -6.215097 | 1.709356 | -2.483821 |
| C | -5.628214 | 0.566955 | -1.970572 |
| C | -4.287774 | 0.801993 | -1.924841 |
| Au | -5.577359 | 4.533880 | -3.535652 |
| C | -5.917148 | 6.431553 | -4.270660 |
| C | -7.234548 | 7.086265 | -3.922528 |
| C | -7.652244 | 1.866484 | -2.690821 |
| C | -2.782581 | 2.717493 | -2.532027 |
| C | -4.982404 | 7.040524 | -5.004924 |
| C | -3.633313 | 6.607231 | -5.471746 |
| O | -5.282965 | 8.453830 | -5.444451 |
| C | -5.277347 | 8.732215 | -6.887857 |
| O | -4.073203 | 10.107504 | -4.047566 |
| S | -2.716721 | 10.688738 | -4.333593 |
| O | -1.918889 | 10.868572 | -3.122520 |
| C | -3.142442 | 12.443174 | -4.878880 |
| F | -3.794606 | 13.099809 | -3.898491 |
| O | -2.056409 | 10.089159 | -5.492930 |
| H | -5.655814 | 9.750385 | -6.999712 |
| H | -5.956211 | 8.014056 | -7.351423 |
| H | -4.700360 | 9.169685 | -4.896702 |
| H | -6.205674 | -0.302367 | -1.685101 |
| H | -3.469003 | 0.177876 | -1.591980 |
| H | -2.844319 | 7.298508 | -5.140087 |
| H | -3.572558 | 6.537070 | -6.567896 |
| H | -3.423083 | 5.613909 | -5.061320 |
| H | -8.070365 | 6.435844 | -4.217897 |
| H | -7.379931 | 8.069646 | -4.388229 |
| H | -7.318510 | 7.207589 | -2.832153 |
| H | -8.180015 | 1.774259 | -1.735257 |
| H | -8.014986 | 1.101888 | -3.386336 |
| H | -7.828765 | 2.859788 | -3.113288 |
| H | -2.931540 | 3.736113 | -2.900936 |
| H | -2.156820 | 2.157616 | -3.235843 |
| H | -2.293225 | 2.751719 | -1.552686 |

H -4.264760 8.640899 -7.290546
F -3.926481 12.415267 -5.975921
F -2.010742 13.114924 -5.172207

**TS_OTf(NM)'**

47

C -3.240644 1.070283 -2.355653
N -3.279702 2.404877 -2.715612
C -4.565963 2.843123 -2.803060
N -5.328657 1.760145 -2.488830
C -4.532275 0.664282 -2.211675
C -2.093004 3.216590 -2.974401
Au -5.205542 4.712160 -3.275499
C -5.937842 6.651687 -3.614403
C -5.425767 7.065771 -4.713840
C -4.591862 6.893688 -5.903680
C -6.788406 1.744002 -2.437007
C -6.868861 7.258216 -2.610293
O -6.046240 8.959171 -5.000969
C -6.531535 9.329022 -6.309133
O -4.042129 10.549015 -4.226705
S -2.639669 10.635661 -4.706275
O -2.287348 9.656300 -5.741031
O -1.657523 10.812697 -3.629806
C -2.613525 12.287455 -5.615350
F -1.383595 12.524125 -6.123390
F -2.930713 13.298861 -4.776326
F -3.502108 12.285010 -6.633842
H -6.885592 10.367241 -6.277005
H -7.369016 8.666703 -6.546792
H -5.249352 9.525045 -4.774587
H -4.947738 -0.296532 -1.938586
H -2.310019 0.531904 -2.235539
H -3.791507 7.644915 -5.946614
H -5.184192 6.949852 -6.826460
H -4.131485 5.897992 -5.866720
H -7.748675 6.617613 -2.467378
H -7.197103 8.253704 -2.928507
H -6.374829 7.338547 -1.632905
H -7.122967 1.523938 -1.417619
H -7.175495 0.984364 -3.124206
H -7.152604 2.730040 -2.738665
H -2.417591 4.236529 -3.198653
H -1.541058 2.809252 -3.828188
H -1.448577 3.224187 -2.089150
H -5.752822 9.231620 -7.076561
O -9.953480 13.080376 -7.004670

| | | | |
|---|---|---|---|
| N | -9.983670 | 14.201240 | -7.521128 |
| O | -9.427556 | 15.197846 | -7.046069 |
| C | -10.727962 | 14.377195 | -8.804557 |
| H | -11.230315 | 13.441137 | -9.044580 |
| H | -11.429719 | 15.202112 | -8.660136 |
| H | -9.988084 | 14.649165 | -9.562805 |

**PC_OTf(NM)'**

47

| | | | |
|---|---|---|---|
| C | -3.097247 | 1.291127 | -2.444134 |
| N | -3.220942 | 2.606069 | -2.856304 |
| C | -4.528659 | 2.993227 | -2.873055 |
| N | -5.216400 | 1.890462 | -2.461371 |
| C | -4.356993 | 0.839404 | -2.194854 |
| C | -2.092489 | 3.454271 | -3.230263 |
| Au | -5.283662 | 4.825400 | -3.398486 |
| C | -6.062069 | 6.676009 | -3.876186 |
| C | -5.601318 | 7.333441 | -4.942663 |
| C | -4.579653 | 6.987522 | -5.972409 |
| C | -6.667670 | 1.814336 | -2.318541 |
| C | -7.128928 | 7.238281 | -2.965896 |
| O | -6.166338 | 8.717709 | -5.175936 |
| C | -6.737342 | 9.016298 | -6.494691 |
| O | -4.782551 | 10.558576 | -4.264695 |
| S | -3.389599 | 10.959605 | -4.658909 |
| O | -2.807707 | 10.121080 | -5.705707 |
| O | -2.548564 | 11.269041 | -3.504184 |
| C | -3.676098 | 12.626551 | -5.491706 |
| F | -2.501260 | 13.120320 | -5.932850 |
| F | -4.217499 | 13.505999 | -4.624366 |
| F | -4.510432 | 12.488846 | -6.543289 |
| H | -7.222744 | 9.991115 | -6.399891 |
| H | -7.473599 | 8.238861 | -6.706838 |
| H | -5.500873 | 9.490823 | -4.844394 |
| H | -4.710411 | -0.125036 | -1.854925 |
| H | -2.137840 | 0.797662 | -2.363583 |
| H | -3.779328 | 7.740518 | -6.018371 |
| H | -5.014117 | 6.899681 | -6.979106 |
| H | -4.138320 | 6.019104 | -5.713305 |
| H | -7.957695 | 6.522608 | -2.869151 |
| H | -7.539795 | 8.199620 | -3.300727 |
| H | -6.727607 | 7.372670 | -1.950679 |
| H | -6.929379 | 1.575811 | -1.282206 |
| H | -7.068669 | 1.043417 | -2.985251 |
| H | -7.087683 | 2.787237 | -2.588813 |
| H | -2.476463 | 4.454404 | -3.451062 |
| H | -1.593544 | 3.046721 | -4.116375 |

| | | | |
|---|---|---|---|
| H | -1.377964 | 3.510796 | -2.402326 |
| H | -5.953350 | 9.037681 | -7.256520 |
| O | -9.187727 | 12.127816 | -6.958040 |
| N | -8.969730 | 13.338962 | -7.065687 |
| O | -8.459084 | 14.032175 | -6.180302 |
| C | -9.335036 | 14.019645 | -8.345118 |
| H | -9.814279 | 13.293196 | -9.000386 |
| H | -9.998532 | 14.849147 | -8.087712 |
| H | -8.407128 | 14.409918 | -8.773595 |

**RC'_OTf(NM)**

47

| | | | |
|---|---|---|---|
| N | -4.572064 | 0.660600 | -2.337097 |
| C | -3.224797 | 0.939990 | -2.443628 |
| C | -3.117585 | 2.271403 | -2.716501 |
| N | -4.401598 | 2.774892 | -2.762035 |
| C | -5.307951 | 1.787652 | -2.530414 |
| C | -4.724293 | 4.169899 | -3.054097 |
| Au | -7.320972 | 1.964858 | -2.496100 |
| C | -9.452629 | 2.004586 | -1.885081 |
| C | -9.426023 | 2.349806 | -3.077382 |
| C | -9.753431 | 2.786722 | -4.435785 |
| C | -5.113330 | -0.658587 | -2.016111 |
| C | -9.852551 | 1.639764 | -0.524253 |
| O | -13.752341 | 1.341997 | -3.045513 |
| C | -14.053440 | 1.161098 | -4.435641 |
| O | -13.653845 | 4.067919 | -2.384702 |
| S | -13.255185 | 5.190346 | -3.262579 |
| O | -12.553660 | 6.279264 | -2.570121 |
| C | -14.909660 | 5.964608 | -3.731311 |
| F | -15.574856 | 6.379094 | -2.627181 |
| O | -12.684671 | 4.786936 | -4.554978 |
| F | -15.692054 | 5.075472 | -4.385027 |
| F | -14.723962 | 7.035766 | -4.538222 |
| O | -8.987817 | 8.452773 | 0.603038 |
| N | -8.641999 | 8.978861 | -0.460979 |
| C | -9.367712 | 10.208355 | -0.903848 |
| O | -7.718172 | 8.566628 | -1.169755 |
| H | -15.041576 | 1.572422 | -4.698297 |
| H | -14.062809 | 0.082639 | -4.633372 |
| H | -13.670409 | 2.310032 | -2.877487 |
| H | -2.466594 | 0.178913 | -2.316629 |
| H | -2.248658 | 2.893779 | -2.882599 |
| H | -10.797945 | 3.129724 | -4.455027 |
| H | -9.630443 | 1.966102 | -5.153528 |
| H | -9.116375 | 3.620284 | -4.755464 |
| H | -9.567013 | 0.607000 | -0.289442 |

| | | | |
|---|---|---|---|
| H | -10.944465 | 1.726087 | -0.440966 |
| H | -9.392416 | 2.302175 | 0.218854 |
| H | -4.888343 | -0.911450 | -0.974331 |
| H | -4.670337 | -1.405538 | -2.681604 |
| H | -6.196547 | -0.633679 | -2.163436 |
| H | -5.796353 | 4.315625 | -2.894974 |
| H | -4.471875 | 4.402484 | -4.093881 |
| H | -4.160084 | 4.822972 | -2.381212 |
| H | -13.295136 | 1.629257 | -5.081934 |
| H | -10.371395 | 10.185274 | -0.477553 |
| H | -8.799019 | 11.054915 | -0.504360 |
| H | -9.364090 | 10.230459 | -1.995061 |

**RC'_OTf(GVL)**

55

| | | | |
|---|---|---|---|
| C | -1.212223 | 2.421775 | -4.659531 |
| N | -1.728205 | 3.240025 | -5.616402 |
| C | -2.906821 | 3.807943 | -5.181707 |
| C | -3.132293 | 3.336721 | -3.921175 |
| N | -2.085492 | 2.491364 | -3.618480 |
| C | -1.139589 | 3.460297 | -6.939173 |
| C | -1.954939 | 1.772116 | -2.352301 |
| Au | 0.475275 | 1.319461 | -4.788206 |
| C | 2.587064 | 0.635689 | -4.758890 |
| C | 3.667942 | 1.547102 | -4.377826 |
| C | 1.906530 | -0.338368 | -5.119110 |
| C | 1.436247 | -1.655670 | -5.554001 |
| O | 4.496228 | 4.148813 | -6.880615 |
| S | 3.502885 | 5.177527 | -7.264855 |
| O | 2.160158 | 4.645637 | -7.538724 |
| O | 3.992991 | 6.187996 | -8.210356 |
| C | 3.269761 | 6.151722 | -5.668177 |
| F | 2.354630 | 7.136014 | -5.842042 |
| F | 4.433076 | 6.723506 | -5.278094 |
| F | 2.838294 | 5.350638 | -4.666435 |
| C | 5.389461 | 9.768867 | -8.820310 |
| C | 4.817107 | 11.058605 | -8.269428 |
| O | 5.820956 | 11.911305 | -7.940278 |
| C | 7.139652 | 11.323017 | -8.293954 |
| C | 6.859267 | 9.818923 | -8.396975 |
| O | 3.648058 | 11.372749 | -8.117970 |
| C | 8.157967 | 11.742287 | -7.258915 |
| H | -3.935140 | 3.533811 | -3.223535 |
| H | -3.475129 | 4.494510 | -5.794600 |
| H | 3.748841 | 2.386062 | -5.081162 |
| H | 4.615093 | 0.990152 | -4.387289 |
| H | 3.513185 | 1.949363 | -3.369325 |

| | | | |
|---|---|---|---|
| H | 0.753017 | -2.096838 | -4.818107 |
| H | 2.303412 | -2.320628 | -5.667555 |
| H | 0.915124 | -1.594928 | -6.517022 |
| H | -2.781495 | 1.062254 | -2.243415 |
| H | -1.967897 | 2.485244 | -1.522058 |
| H | -1.004231 | 1.232223 | -2.357874 |
| H | -0.067537 | 3.657408 | -6.839842 |
| H | -1.627409 | 4.326870 | -7.392169 |
| H | -1.300973 | 2.582183 | -7.573160 |
| H | 5.271450 | 9.802297 | -9.913744 |
| H | 4.826819 | 8.903924 | -8.452808 |
| H | 7.537596 | 9.333725 | -9.106579 |
| H | 6.994302 | 9.348715 | -7.413054 |
| H | 7.388822 | 11.741195 | -9.278977 |
| H | 9.135802 | 11.321004 | -7.527983 |
| H | 8.257542 | 12.833657 | -7.217429 |
| H | 7.881653 | 11.367835 | -6.264381 |
| H | 6.253004 | 4.262779 | -7.327319 |
| O | 7.221217 | 4.231213 | -7.516126 |
| C | 7.431997 | 4.797165 | -8.818151 |
| H | 8.513388 | 4.818014 | -8.997381 |
| H | 6.958467 | 4.191925 | -9.607543 |
| H | 7.042188 | 5.824261 | -8.880997 |

**[RC_TCMA]+**

37

| | | | |
|---|---|---|---|
| C | -2.458072 | 8.915970 | -9.375215 |
| N | -2.780562 | 7.599469 | -9.255534 |
| C | -3.300650 | 7.341410 | -8.004404 |
| C | -3.303056 | 8.524063 | -7.326050 |
| N | -2.784326 | 9.475621 | -8.179029 |
| C | -2.612051 | 6.586387 | -10.295484 |
| C | -2.627530 | 10.886438 | -7.830876 |
| Au | -1.684023 | 9.841191 | -10.995655 |
| C | -0.303766 | 10.696909 | -12.510097 |
| C | 1.147193 | 10.616575 | -12.333986 |
| C | -1.456160 | 10.911596 | -12.919082 |
| C | -2.633986 | 11.322636 | -13.686719 |
| O | 3.001114 | 11.895008 | -15.072741 |
| C | 2.345894 | 12.935282 | -15.825019 |
| Cl | 3.655032 | 9.123963 | -17.088965 |
| C | 5.433975 | 8.947907 | -17.296830 |
| Cl | 6.257547 | 8.886996 | -15.717264 |
| Cl | 6.087610 | 10.254121 | -18.319222 |
| H | 2.147590 | 13.754864 | -15.125827 |
| H | 1.390883 | 12.589449 | -16.247605 |
| H | 3.176389 | 11.151741 | -15.680173 |

| | | | |
|---|---|---|---|
| H | -3.624871 | 8.763704 | -6.321667 |
| H | -3.620061 | 6.352170 | -7.704869 |
| H | -3.240736 | 12.043494 | -13.125746 |
| H | -3.264450 | 10.461687 | -13.940035 |
| H | -2.302442 | 11.798101 | -14.619426 |
| H | 1.472213 | 11.205049 | -11.466453 |
| H | 1.639939 | 11.016858 | -13.233668 |
| H | 1.474539 | 9.579784 | -12.186717 |
| H | -2.020529 | 10.974633 | -6.925067 |
| H | -3.610751 | 11.337331 | -7.661759 |
| H | -2.128040 | 11.394641 | -8.659766 |
| H | -2.158562 | 7.061118 | -11.169633 |
| H | -3.587282 | 6.170001 | -10.567545 |
| H | -1.958396 | 5.788338 | -9.930181 |
| H | 2.984389 | 13.311933 | -16.637803 |
| H | 5.599761 | 8.000938 | -17.805574 |

**[TS_TCMA]+**

37

| | | | |
|---|---|---|---|
| N | -3.443412 | 8.192020 | -9.741654 |
| C | -4.324403 | 8.120612 | -8.678021 |
| C | -4.016025 | 9.150763 | -7.842818 |
| N | -2.955133 | 9.826266 | -8.417263 |
| C | -2.591660 | 9.244090 | -9.593448 |
| C | -2.318999 | 11.001028 | -7.826693 |
| Au | -1.102999 | 9.831320 | -10.849015 |
| C | 0.494387 | 10.486785 | -12.028592 |
| C | 0.256381 | 10.299547 | -13.284472 |
| O | 1.707567 | 10.910873 | -14.318691 |
| C | 1.474640 | 12.174446 | -15.010440 |
| C | -3.447097 | 7.263538 | -10.868957 |
| C | 1.685109 | 11.083756 | -11.336598 |
| C | -0.658853 | 9.795929 | -14.317189 |
| Cl | 2.643439 | 8.625353 | -16.458745 |
| C | 4.338452 | 9.147608 | -16.818780 |
| H | 1.291290 | 12.920532 | -14.234964 |
| H | 0.613437 | 12.102823 | -15.683590 |
| H | 1.915655 | 10.210802 | -14.984021 |
| H | -4.452889 | 9.456092 | -6.901383 |
| H | -5.083384 | 7.352914 | -8.607658 |
| H | -1.578166 | 9.454572 | -13.825609 |
| H | -0.233814 | 8.942722 | -14.863815 |
| H | -0.939269 | 10.574999 | -15.038031 |
| H | 1.384201 | 11.968339 | -10.759495 |
| H | 2.470197 | 11.371750 | -12.044767 |
| H | 2.102532 | 10.368060 | -10.616153 |
| H | -1.899190 | 10.744635 | -6.848167 |

| | | | |
|---|---|---|---|
| H | -3.054244 | 11.804687 | -7.713417 |
| H | -1.518345 | 11.329525 | -8.495264 |
| H | -2.599217 | 7.506301 | -11.515357 |
| H | -4.381178 | 7.362422 | -11.432358 |
| H | -3.345167 | 6.236902 | -10.502510 |
| H | 2.378763 | 12.429366 | -15.572617 |
| H | 4.809240 | 8.316527 | -17.340211 |
| Cl | 4.343085 | 10.569372 | -17.887192 |
| Cl | 5.232352 | 9.459872 | -15.313811 |

**[PC_TCMA]+**

37

| | | | |
|---|---|---|---|
| N | -3.429594 | 8.216276 | -9.777868 |
| C | -4.318700 | 8.148044 | -8.720562 |
| C | -4.009335 | 9.175138 | -7.881896 |
| N | -2.939551 | 9.843256 | -8.448864 |
| C | -2.568624 | 9.261728 | -9.624638 |
| C | -2.301511 | 11.014929 | -7.854596 |
| Au | -1.057144 | 9.839370 | -10.876888 |
| C | 0.504514 | 10.457877 | -12.081140 |
| C | 0.397947 | 10.295430 | -13.392286 |
| O | 1.627321 | 10.803958 | -14.239608 |
| C | 1.448786 | 12.112957 | -14.912944 |
| C | -3.429209 | 7.287826 | -10.905151 |
| C | 1.699999 | 11.080790 | -11.403262 |
| C | -0.614624 | 9.726453 | -14.318839 |
| Cl | 2.558582 | 8.688577 | -16.354014 |
| C | 4.256053 | 9.219880 | -16.737323 |
| H | 1.331096 | 12.842640 | -14.112006 |
| H | 0.569946 | 12.077881 | -15.560660 |
| H | 1.891433 | 10.109174 | -14.912128 |
| H | -4.451314 | 9.482304 | -6.943296 |
| H | -5.083226 | 7.385101 | -8.656250 |
| H | -1.481201 | 9.406059 | -13.730420 |
| H | -0.231600 | 8.848062 | -14.860668 |
| H | -0.962036 | 10.458669 | -15.061739 |
| H | 1.395266 | 11.991881 | -10.868484 |
| H | 2.517457 | 11.339657 | -12.088299 |
| H | 2.095311 | 10.398266 | -10.638146 |
| H | -1.899685 | 10.760665 | -6.867841 |
| H | -3.029878 | 11.827245 | -7.757051 |
| H | -1.487340 | 11.330826 | -8.513075 |
| H | -2.586493 | 7.540601 | -11.554600 |
| H | -4.366524 | 7.377411 | -11.465055 |
| H | -3.315009 | 6.261410 | -10.541016 |
| H | 2.363471 | 12.293835 | -15.481472 |
| H | 4.715254 | 8.379489 | -17.254288 |

| | | | |
|---|---|---|---|
| Cl | 4.236785 | 10.624913 | -17.821104 |
| Cl | 5.158280 | 9.549027 | -15.245613 |

**[RC_NM]+**

39

| | | | |
|---|---|---|---|
| N | -2.578709 | 7.841157 | -9.467092 |
| C | -3.370097 | 7.648157 | -8.354161 |
| C | -3.466816 | 8.853504 | -7.724150 |
| N | -2.735055 | 9.754197 | -8.469217 |
| C | -2.180725 | 9.139624 | -9.549107 |
| C | -2.571209 | 11.163450 | -8.117305 |
| Au | -1.007768 | 9.969594 | -10.969464 |
| C | 0.736929 | 10.755497 | -12.090887 |
| C | -0.248262 | 10.893733 | -12.834220 |
| C | -1.151802 | 11.192101 | -13.948136 |
| C | -2.247543 | 6.789653 | -10.426764 |
| C | 2.075853 | 10.748020 | -11.498189 |
| O | 4.563142 | 11.308516 | -14.006072 |
| C | 4.128850 | 12.240211 | -15.010006 |
| O | 4.379960 | 8.532425 | -14.798682 |
| N | 4.915883 | 8.200031 | -15.869043 |
| O | 5.311280 | 8.997979 | -16.717012 |
| C | 5.109943 | 6.740414 | -16.108362 |
| H | 4.362748 | 13.246020 | -14.644196 |
| H | 3.043824 | 12.174748 | -15.184608 |
| H | 4.469803 | 10.401298 | -14.372686 |
| H | -3.985748 | 9.141416 | -6.819826 |
| H | -3.792772 | 6.683498 | -8.107522 |
| H | -1.940010 | 11.891128 | -13.645346 |
| H | -1.627233 | 10.280423 | -14.330044 |
| H | -0.573543 | 11.651023 | -14.761669 |
| H | 2.141724 | 11.459872 | -10.665828 |
| H | 2.808937 | 11.035109 | -12.268497 |
| H | 2.340955 | 9.753187 | -11.120111 |
| H | -2.038169 | 11.246782 | -7.164774 |
| H | -3.554269 | 11.637263 | -8.033711 |
| H | -1.992683 | 11.652122 | -8.905949 |
| H | -1.519624 | 7.187200 | -11.139362 |
| H | -3.150682 | 6.475288 | -10.960148 |
| H | -1.814686 | 5.935098 | -9.897644 |
| H | 4.652968 | 12.082866 | -15.963923 |
| H | 4.214926 | 6.222851 | -15.758460 |
| H | 5.299627 | 6.591373 | -17.171114 |
| H | 5.975846 | 6.445712 | -15.506938 |

**[TS_NM]+**

39

| | | | |
|---|---|---|---|
| C | -3.988919 | 8.128842 | -8.850426 |
| C | -3.745742 | 9.127881 | -7.957762 |
| N | -2.638853 | 9.815546 | -8.420197 |
| C | -2.182325 | 9.269949 | -9.580877 |
| N | -3.023039 | 8.229406 | -9.834935 |
| C | -2.043194 | 10.960363 | -7.735637 |
| Au | -0.575238 | 9.864698 | -10.672505 |
| C | 1.173592 | 10.481338 | -11.653813 |
| C | 2.361566 | 10.858070 | -10.821481 |
| C | -2.939850 | 7.341222 | -10.991592 |
| C | 0.973212 | 10.432008 | -12.921474 |
| C | 0.103776 | 10.181856 | -14.073528 |
| O | 2.660801 | 10.909200 | -13.836366 |
| C | 2.612806 | 11.931364 | -14.861577 |
| O | 3.377024 | 8.411712 | -14.738352 |
| N | 4.398215 | 8.303556 | -15.446197 |
| C | 4.815282 | 6.926205 | -15.830635 |
| O | 5.076865 | 9.256206 | -15.814134 |
| H | 2.207572 | 12.833813 | -14.396371 |
| H | 1.981416 | 11.628589 | -15.705793 |
| H | 2.968229 | 10.049366 | -14.238908 |
| H | -4.257449 | 9.404417 | -7.045614 |
| H | -4.755614 | 7.365713 | -8.869413 |
| H | -0.889238 | 9.896964 | -13.703634 |
| H | 0.481860 | 9.365917 | -14.703616 |
| H | -0.020694 | 11.079159 | -14.693437 |
| H | 2.099695 | 11.667906 | -10.128192 |
| H | 3.200798 | 11.179799 | -11.447721 |
| H | 2.679626 | 10.006779 | -10.205069 |
| H | -1.641218 | 10.648543 | -6.765652 |
| H | -2.800330 | 11.737287 | -7.587936 |
| H | -1.234716 | 11.350694 | -8.360123 |
| H | -2.041918 | 7.600687 | -11.559204 |
| H | -3.825368 | 7.466232 | -11.624047 |
| H | -2.871613 | 6.301380 | -10.655548 |
| H | 3.633269 | 12.124552 | -15.213110 |
| H | 3.925192 | 6.297968 | -15.864143 |
| H | 5.334289 | 6.989369 | -16.787281 |
| H | 5.497974 | 6.587450 | -15.044321 |

**[PC_NM]+**

39

| | | | |
|---|---|---|---|
| N | -3.494937 | 8.317474 | -9.847215 |
| C | -4.357198 | 8.219262 | -8.770241 |
| C | -3.950892 | 9.144730 | -7.857984 |

| | | | |
|---|---|---|---|
| N | -2.852006 | 9.784089 | -8.402460 |
| C | -2.556158 | 9.283353 | -9.635747 |
| C | -2.114563 | 10.852410 | -7.733160 |
| Au | -1.039134 | 9.862445 | -10.885859 |
| C | 0.523609 | 10.473161 | -12.088109 |
| C | 0.447061 | 10.310760 | -13.408202 |
| O | 1.653381 | 10.786101 | -14.223685 |
| C | 1.479059 | 12.044517 | -14.975087 |
| C | -3.592560 | 7.492212 | -11.047935 |
| C | 1.716438 | 11.100077 | -11.405502 |
| C | -0.587154 | 9.737404 | -14.314489 |
| O | 2.552075 | 8.791355 | -15.607451 |
| N | 3.529878 | 9.037266 | -16.358092 |
| O | 3.990823 | 10.155698 | -16.520308 |
| C | 4.151483 | 7.872580 | -17.039997 |
| H | 1.280633 | 12.818000 | -14.232133 |
| H | 0.651827 | 11.945074 | -15.682424 |
| H | 2.014413 | 10.029401 | -14.833626 |
| H | -4.343876 | 9.398595 | -6.882317 |
| H | -5.173087 | 7.509140 | -8.744942 |
| H | -1.432768 | 9.396247 | -13.707907 |
| H | -0.204300 | 8.877934 | -14.884899 |
| H | -0.966463 | 10.474763 | -15.037198 |
| H | 1.404684 | 11.998534 | -10.852929 |
| H | 2.527214 | 11.380548 | -12.090309 |
| H | 2.125440 | 10.410558 | -10.652869 |
| H | -1.695569 | 10.483514 | -6.790772 |
| H | -2.781650 | 11.697706 | -7.533083 |
| H | -1.304729 | 11.173224 | -8.394364 |
| H | -2.760316 | 7.751875 | -11.707826 |
| H | -4.542334 | 7.684212 | -11.558749 |
| H | -3.528387 | 6.432719 | -10.778187 |
| H | 2.424513 | 12.223479 | -15.490887 |
| H | 3.367855 | 7.143519 | -17.246721 |
| H | 4.649565 | 8.239158 | -17.937294 |
| H | 4.878164 | 7.462241 | -16.329978 |

**[RC_GVL]+**

47

| | | | |
|---|---|---|---|
| C | -1.078622 | 14.110196 | -2.829926 |
| C | -1.528569 | 15.072890 | -1.755365 |
| O | -0.663323 | 15.068658 | -0.722557 |
| C | 0.484591 | 14.160700 | -0.996422 |
| C | -0.023115 | 13.249978 | -2.128902 |
| O | -2.516569 | 15.797569 | -1.739131 |
| C | 1.701801 | 14.999354 | -1.336729 |
| O | -4.371559 | 15.949828 | -3.818996 |

| | | | |
|---|---|---|---|
| C | -5.140755 | 17.140087 | -3.591875 |
| C | -7.070772 | 13.303095 | -0.681405 |
| C | -6.926318 | 13.716078 | 0.717186 |
| C | -6.955933 | 13.175164 | -1.911333 |
| C | -6.579412 | 13.293846 | -3.320502 |
| Au | -8.494072 | 11.709847 | -1.257215 |
| C | -9.900851 | 10.258552 | -1.220979 |
| N | -11.228836 | 10.392624 | -1.486219 |
| C | -11.872029 | 9.179047 | -1.356851 |
| C | -10.924721 | 8.266256 | -0.997921 |
| N | -9.725324 | 8.943362 | -0.920827 |
| C | -11.894370 | 11.634817 | -1.874956 |
| C | -8.456299 | 8.318901 | -0.552066 |
| H | -5.708417 | 17.086133 | -2.649397 |
| H | -5.851203 | 17.236703 | -4.421189 |
| H | -3.717633 | 15.869725 | -3.082389 |
| H | -11.002245 | 7.206564 | -0.795972 |
| H | -12.933961 | 9.068050 | -1.530020 |
| H | -7.886849 | 14.027522 | 1.145623 |
| H | -6.231177 | 14.565327 | 0.767014 |
| H | -6.522536 | 12.900970 | 1.330608 |
| H | -6.131411 | 12.363330 | -3.691324 |
| H | -5.843766 | 14.108406 | -3.426047 |
| H | -7.449958 | 13.527114 | -3.945728 |
| H | -8.233612 | 7.502101 | -1.245642 |
| H | -8.519159 | 7.929131 | 0.469049 |
| H | -7.669079 | 9.075267 | -0.609351 |
| H | -11.176774 | 12.454967 | -1.786183 |
| H | -12.743339 | 11.816985 | -1.209466 |
| H | -12.244379 | 11.561636 | -2.909780 |
| H | -4.505198 | 18.039047 | -3.569870 |
| H | -1.930243 | 13.552026 | -3.231471 |
| H | -0.664304 | 14.707037 | -3.655087 |
| H | -0.484260 | 12.347949 | -1.710302 |
| H | 0.791949 | 12.941848 | -2.791402 |
| H | 0.637190 | 13.616887 | -0.058911 |
| H | 1.915074 | 15.719531 | -0.537861 |
| H | 2.572266 | 14.339829 | -1.445397 |
| H | 1.562095 | 15.545570 | -2.279005 |

**[TS_GVL]+**

47

| | | | |
|---|---|---|---|
| N | -10.719479 | 10.900305 | -1.459089 |
| C | -9.365937 | 10.754897 | -1.480407 |
| N | -9.139178 | 9.499850 | -1.003672 |
| C | -10.330594 | 8.874029 | -0.687182 |
| C | -11.326930 | 9.756845 | -0.974411 |

| | | | |
|---|---|---|---|
| Au | -7.986511 | 12.104767 | -2.112904 |
| C | -6.573627 | 13.426801 | -2.932822 |
| C | -6.251990 | 13.331890 | -4.391366 |
| C | -7.824395 | 8.883421 | -0.843786 |
| C | -11.445800 | 12.095245 | -1.881953 |
| C | -6.163726 | 14.177017 | -1.980115 |
| C | -6.144211 | 14.623780 | -0.586280 |
| O | -4.780635 | 15.448926 | -2.741210 |
| C | -5.252628 | 16.803829 | -2.905061 |
| O | -2.694662 | 15.480642 | -1.077023 |
| C | -1.653269 | 14.872546 | -1.323908 |
| O | -0.624121 | 14.918631 | -0.469193 |
| C | 0.545080 | 14.161021 | -1.003951 |
| C | -0.060399 | 13.267995 | -2.102056 |
| C | -1.319570 | 14.028208 | -2.530010 |
| C | 1.591650 | 15.151720 | -1.474691 |
| H | -5.611600 | 17.225520 | -1.956373 |
| H | -6.071927 | 16.779374 | -3.629205 |
| H | -3.999759 | 15.451247 | -2.106416 |
| H | -10.365985 | 7.868416 | -0.289938 |
| H | -12.400877 | 9.671757 | -0.876564 |
| H | -6.888381 | 14.047698 | -0.021155 |
| H | -6.406586 | 15.686112 | -0.496216 |
| H | -5.162918 | 14.461573 | -0.121553 |
| H | -5.903986 | 12.321569 | -4.642731 |
| H | -5.479066 | 14.057048 | -4.669898 |
| H | -7.151566 | 13.514064 | -4.994008 |
| H | -7.755617 | 7.986436 | -1.468273 |
| H | -7.666115 | 8.613736 | 0.205564 |
| H | -7.066520 | 9.607551 | -1.155781 |
| H | -10.717189 | 12.838222 | -2.218391 |
| H | -12.020297 | 12.497688 | -1.041012 |
| H | -12.123995 | 11.845921 | -2.704804 |
| H | -4.438022 | 17.427005 | -3.295327 |
| H | -2.166696 | 13.390270 | -2.801943 |
| H | -1.141682 | 14.710081 | -3.374531 |
| H | -0.329661 | 12.289651 | -1.688300 |
| H | 0.645485 | 13.111003 | -2.923565 |
| H | 0.910445 | 13.583313 | -0.149554 |
| H | 1.867918 | 15.841017 | -0.667871 |
| H | 2.491485 | 14.601923 | -1.779184 |
| H | 1.235522 | 15.734787 | -2.334506 |

**[PC_GVL]+**

47

| | | | |
|---|---|---|---|
| C | -2.360809 | 9.946604 | -8.247702 |
| C | -3.541040 | 9.352879 | -7.528642 |

| | | | |
|---|---|---|---|
| O | -4.205699 | 8.498702 | -8.283391 |
| C | -3.543163 | 8.350100 | -9.623757 |
| C | -2.618889 | 9.577052 | -9.713393 |
| O | -3.921944 | 9.566351 | -6.362523 |
| C | -2.852954 | 7.003035 | -9.667050 |
| O | -2.612830 | 11.097180 | -4.940729 |
| C | -2.524110 | 10.564800 | -3.573367 |
| C | -3.012102 | 12.546971 | -5.060937 |
| C | -4.483778 | 12.703434 | -4.867019 |
| C | -2.041900 | 13.426155 | -5.322442 |
| C | -0.595876 | 13.015254 | -5.476587 |
| Au | -2.484781 | 15.431486 | -5.520665 |
| C | -2.870115 | 17.435594 | -5.730905 |
| N | -2.952199 | 18.378542 | -4.749213 |
| C | -3.228733 | 19.625903 | -5.279949 |
| C | -3.323045 | 19.465052 | -6.628827 |
| N | -3.101280 | 18.123591 | -6.885325 |
| C | -2.778526 | 18.117765 | -3.322569 |
| C | -3.118295 | 17.533153 | -8.221298 |
| H | -3.484857 | 10.675598 | -3.062063 |
| H | -1.738374 | 11.124792 | -3.062874 |
| H | -3.202868 | 10.441346 | -5.587691 |
| H | -3.525279 | 20.178569 | -7.416641 |
| H | -3.332036 | 20.507537 | -4.661216 |
| H | -4.742984 | 13.762973 | -4.968345 |
| H | -4.811509 | 12.366957 | -3.871876 |
| H | -5.059255 | 12.134564 | -5.613056 |
| H | -0.207124 | 13.354322 | -6.447693 |
| H | -0.427856 | 11.932682 | -5.398582 |
| H | 0.021724 | 13.514625 | -4.715474 |
| H | -2.357893 | 18.009425 | -8.849636 |
| H | -4.105700 | 17.666235 | -8.676625 |
| H | -2.899350 | 16.465886 | -8.123603 |
| H | -2.553278 | 17.054857 | -3.196333 |
| H | -3.698724 | 18.365502 | -2.782307 |
| H | -1.950580 | 18.719023 | -2.931704 |
| H | -2.252047 | 9.511029 | -3.669980 |
| H | -2.285044 | 11.022304 | -8.054871 |
| H | -1.452709 | 9.478776 | -7.838981 |
| H | -3.128050 | 10.399292 | -10.227831 |
| H | -1.699988 | 9.344648 | -10.260235 |
| H | -4.372459 | 8.393500 | -10.335069 |
| H | -3.560203 | 6.193545 | -9.450719 |
| H | -2.450570 | 6.846658 | -10.676066 |
| H | -2.021466 | 6.952902 | -8.951624 |